# VI. ENVIRONMENTAL RECEPTORS AND EFFECTS OF AIR QUALITY

## A. PURPOSE

The purpose of this section is to describe the current status of air quality related values (AQRVs) in Shenandoah National Park (SHEN), trends in resource conditions, and available data regarding air pollution dose-response relationships. Information is presented for aquatic, vegetation, and visibility resources.

## B. AQUATIC ECOSYSTEMS

### 1. Current Status of Streamwater Chemistry

Information concerning the status of streams within SHEN relative to acidic deposition was provided through the Shenandoah Watershed Study (SWAS), a cooperative program of the Department of Environmental Sciences at the University of Virginia and the National Park Service (NPS). The primary scientific objective of the SWAS program has been to improve understanding of watershed processes and hydro-biogeochemical conditions in forested watersheds in SHEN and within the larger central Appalachian Mountain region. The primary on-going resource management objective is to detect and assess hydro-biogeochemical changes that are occurring in relatively pristine ecosystems in response to acidic deposition.

The SWAS program was initiated in 1979, with the establishment of water quality monitoring on two streams (Webb et al. 1993). The current watershed data collection involves 14 primary study watersheds (Figure VI-1), including a combination of discharge gauging, routine quarterly and weekly water quality sampling, and high-frequency episodic, or storm-flow, sampling (Galloway et al. 1999). In addition, a number of extensive stream chemistry surveys, fish population surveys, and other watershed data collection efforts have been conducted throughout the park in support of various research efforts. The SWAS program is presently coordinated with the Virginia Trout Stream Sensitivity Study (VTSSS), which extends quarterly sampling to an additional 51 native brook trout (*Salvelinus fontinalis*) streams located on public lands throughout western Virginia (primarily in the George Washington and Jefferson National Forests).

Aquatic effects research at SHEN has contributed significantly to the development of scientific understanding of watershed processes that control aquatic effects of acidic deposition

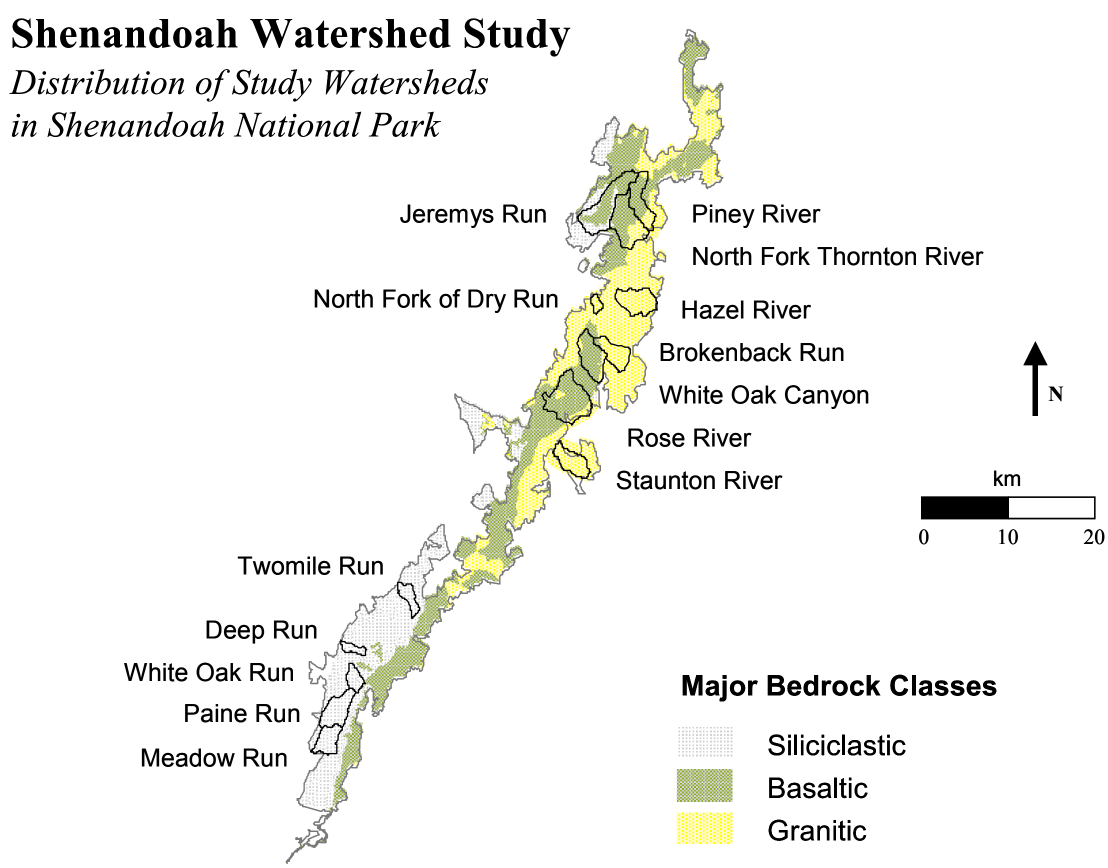



Figure VI-1. Primary study watersheds in SHEN shown in relation to the distribution of major bedrock types.

(c.f., Galloway et al. 1983, 1984). In particular, this research has contributed to our understanding of relationships between geology and sensitivity to acidification (Lynch and Dise 1985, Bricker and Rice 1989) and of the effects of forest insect infestation on episodic chemical processes (Webb et al. 1995, Eshleman et al. 2001). The MAGIC model (Cosby et al. 1985a,b,c) of watershed response was initially developed largely using data collected within SHEN. MAGIC was the principal model used by the National Acid Precipitation Assessment Program (NAPAP) to estimate future damage to lakes and streams in the eastern United States (Thornton et al. 1990, NAPAP 1991) and is now the most widely used acid-base chemistry model in the United States and Europe (Sullivan 2000).

During the past two decades, the SWAS program has developed a uniquely comprehensive watershed database for SHEN, while making major contributions to scientific understanding of surface water acidification and the biogeochemistry of forested mountain watersheds. Data and analyses provided through SWAS have contributed significantly to regional and national assessments of acidic deposition effects, including several that led to enactment of the Clean Air Act Amendments (CAAA) of 1990 (e.g., Baker et al. 1990b, NAPAP 1991, Cosby et al. 1991). More recently, the SWAS and VTSSS programs have provided some of the most comprehensive data available for use in the aquatic effects assessment conducted as part of the Southern Appalachian Mountain Initiative (SAMI), a multistate, multiagency effort to address the air pollution problem in the southern Appalachian region (Sullivan et al. 2002a). The combined SWAS and VTSSS programs presently contribute data to the U.S. Environmental Protection Agency (EPA) for use in Congressionally mandated evaluation of air pollution control program benefits relative to acidic-deposition effects on sensitive surface waters. As a consequence of this extensive monitoring, research, and assessment activity, SHEN is a leader among the national parks with respect to park-specific knowledge of acidic deposition effects and watershed ecosystem conditions in general.

Sulfur (S) is the primary determinant of precipitation acidity and sulfate ($SO_4^{2-}$) is the dominant acid anion associated with acidic streams, both in the central Appalachian Mountains region and within SHEN. Although a substantial proportion of atmospherically deposited S is retained in watershed soils, $SO_4^{2-}$ concentrations in western Virginia mountain streams appear to have increased dramatically as a consequence of acidic deposition. Elevated streamwater $SO_4^{2-}$ concentrations, low acid neutralizing capacity (ANC), and the base-poor status of watershed soils provide evidence of acidification of a substantial portion of the mountain streams in SHEN and among native brook trout streams throughout western Virginia. Such acidification is partly a consequence of past and current S deposition.

Nitrate ($NO_3^-$) concentrations measured in streamwater are generally negligible, except in association with forest defoliation by the gypsy moth (*Lymantria dispar*; Webb et al. 1995; Eshleman et al. 1998, 2001). In the absence of severe disturbance, nitrogen (N) is generally tightly cycled within SHEN watersheds and does not contribute significantly to streamwater acidification. This is likely a consequence of the 1) observation that levels of N deposition in SHEN are lower than in other forested areas with documented effects on streamwaters, 2) past landscape disturbance, and 3) prevalence of deciduous forest types, which seem to have a higher N demand than coniferous forests.

The distributions of streamwater ANC, $SO_4^{2-}$, and sum of base cation concentrations for the streams that have been recently monitored in SHEN are given in Table VI-1. There are large differences (i.e., up to a factor of three among monitored sites) in median streamwater $SO_4^{2-}$ concentrations. There are also distinct patterns in the distribution of sites having high versus low streamwater $SO_4^{2-}$ concentration, despite the fact that S deposition appears to be relatively uniform across the park (Galloway et al. 1999). Data for all quarterly samples during all seasons are summarized in Table VI-1a. In the following tables (VI-1b through VI-1e), quarterly data for each season are presented separately. Sulfate concentrations tend to be higher and ANC values tend to be lower during winter and spring than during summer and fall. Site location information and ANC summary data for most of the streams (n = 297) sampled in SHEN through the SWAS program during the 1980-2001 water-year period are provided in Appendix D.

With the exception of three previously established weekly sampling sites, the primary SWAS watersheds shown in Figure VI-1 were selected for quarterly streamwater sampling following a near-census sampling survey (n = 344) of western Virginia's native brook trout streams conducted in 1987 through the VTSSS program. Results of the VTSSS survey were reported by Webb et al. (1989) and Cosby et al. (1991) and incorporated into regional analyses by Baker et al. (1990a) and Herlihy et al. (1993). In addition to providing a baseline against which to measure future change, the VTSSS survey revealed the sensitivity of many of the region's mountain headwater streams to the effects of acidic deposition. Following the survey, a subset of surveyed streams was selected for continued long-term water quality monitoring.

Selection of the long-term monitoring streams, including those presently maintained by the SWAS program in SHEN and by the VTSSS program in the larger western Virginia area, involved systematic identification of geologically-representative streams with minimal current watershed disturbance. The objective was to select the subset of second or third order streams that most closely represented the range of regional variation in watershed responsiveness to acidic deposition effects, while minimizing the confounding influence of other anthropogenic factors. Within SHEN, the process essentially involved selection of all the second or third order streams that met the disturbance criteria. That is, most of the park's larger streams were selected

Table VI-1 a. Interquartile distributions of ANC, sulfate and sum of base cations (Ca+Mg+Na+K) for SHEN study streams during the period 1988 to 2001 for ALL quarterly samples.[a]

| Site ID | Watershed | Percent of Watershed Area | | | ANC (ueq/L) | | | SO4 (ueq/L) | | | SBC (ueq/L) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Siliciclastic | Granitic | Basaltic | 25th | median | 75th | 25th | median | 75th | 25th | median | 75th |
| **Siliciclastic Bedrock Class** | | | | | | | | | | | | | |
| DR01 | Deep Run | 100 | 0 | 0 | 0.3 | 1.9 | 5.1 | 88.8 | 102.0 | 107.3 | 129.7 | 132.7 | 137.4 |
| PAIN | Paine Run | 100 | 0 | 0 | 2.9 | 6.4 | 10.6 | 106.4 | 110.8 | 115.5 | 144.9 | 150.1 | 156.6 |
| VT36 | Meadow Run | 100 | 0 | 0 | -3.9 | -1.3 | 1.0 | 78.3 | 87.3 | 92.6 | 108.3 | 113.1 | 118.3 |
| VT53 | Twomile Run | 100 | 0 | 0 | 9.4 | 12.8 | 22.8 | 88.9 | 98.3 | 104.1 | 139.4 | 143.1 | 147.8 |
| WOR1 | White Oak Run | 100 | 0 | 0 | 15.7 | 21.6 | 39.7 | 73.9 | 77.8 | 81.9 | 134.9 | 148.2 | 167.2 |
| **Granitic Bedrock Class** | | | | | | | | | | | | | |
| NFDR | North Fork Dry Run | 0 | 100 | 0 | 45.1 | 59.5 | 83.4 | 92.9 | 97.5 | 101.7 | 209.2 | 223.7 | 252.7 |
| VT58 | Brokenback Run | 0 | 93 | 7 | 66.8 | 83.6 | 108.9 | 37.5 | 41.4 | 44.9 | 152.5 | 165.9 | 185.8 |
| STAN | Staunton River | 0 | 100 | 0 | 73.6 | 81.4 | 101.2 | 39.7 | 42.4 | 45.4 | 154.8 | 161.1 | 177.7 |
| VT62 | Hazel River | 0 | 100 | 0 | 77.7 | 93.0 | 112.1 | 33.8 | 38.3 | 41.8 | 163.9 | 175.8 | 196.0 |
| **Basaltic Bedrock Class** | | | | | | | | | | | | | |
| VT51 | Jeremys Run | 31 | 0 | 69 | 140.6 | 179.5 | 260.1 | 105.0 | 119.2 | 130.0 | 328.3 | 366.6 | 408.6 |
| PINE | Piney River | 0 | 31 | 69 | 166.2 | 207.4 | 300.4 | 54.0 | 62.5 | 69.4 | 311.7 | 341.3 | 396.5 |
| VT61 | North Fork Thornton River | 5 | 27 | 68 | 217.3 | 266.5 | 363.6 | 67.5 | 78.8 | 92.4 | 381.0 | 416.1 | 478.0 |
| VT66 | Rose River | 0 | 9 | 91 | 112.8 | 141.6 | 186.2 | 47.1 | 51.3 | 57.6 | 243.9 | 265.1 | 294.3 |
| VT75 | White Oak Canyon Run | 0 | 14 | 86 | 101.7 | 130.4 | 172.7 | 45.4 | 51.4 | 58.3 | 221.9 | 247.8 | 275.2 |

[a] The data cover 14 water years except for VT75 (11 years)

Table VI-1 b. Interquartile distributions of ANC, sulfate and sum of base cations (Ca+Mg+Na+K) for SHEN study streams during the period 1988 to 2001 for WINTER quarterly samples (sampled in the last week of January). [a]

| Site ID | Watershed | Percent of Watershed Area | | | ANC (ueq/L) | | | SO4 (ueq/L) | | | SBC (ueq/L) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Siliciclastic | Granitic | Basaltic | 25th | median | 75th | 25th | median | 75th | 25th | median | 75th |
| **Siliciclastic Bedrock Class** | | | | | | | | | | | | | |
| DR01 | Deep Run | 100 | 0 | 0 | -0.4 | 0.3 | 1.7 | 105.3 | 108.9 | 111.2 | 133.8 | 137.4 | 137.7 |
| PAIN | Paine Run | 100 | 0 | 0 | 1.2 | 2.9 | 4.4 | 110.2 | 113.9 | 116.1 | 144.8 | 149.5 | 155.3 |
| VT36 | Meadow Run | 100 | 0 | 0 | -4.6 | -2.4 | -0.8 | 89.4 | 92.3 | 101.8 | 115.3 | 118.2 | 124.6 |
| VT53 | Twomile Run | 100 | 0 | 0 | 4.6 | 7.8 | 10.3 | 100.3 | 105.7 | 108.6 | 141.1 | 143.9 | 147.5 |
| WOR1 | White Oak Run | 100 | 0 | 0 | 13.1 | 15.3 | 17.1 | 74.1 | 79.6 | 82.5 | 132.1 | 133.9 | 148.0 |
| **Granitic Bedrock Class** | | | | | | | | | | | | | |
| NFDR | North Fork Dry Run | 0 | 100 | 0 | 32.4 | 35.3 | 44.1 | 96.8 | 101.1 | 110.1 | 194.4 | 207.4 | 225.5 |
| VT58 | Brokenback Run | 0 | 93 | 7 | 49.4 | 57.9 | 65.6 | 42.7 | 45.3 | 51.4 | 140.7 | 146.2 | 156.8 |
| STAN | Staunton River | 0 | 100 | 0 | 68.0 | 71.2 | 74.4 | 42.3 | 47.0 | 50.0 | 152.2 | 153.3 | 157.4 |
| VT62 | Hazel River | 0 | 100 | 0 | 59.5 | 65.8 | 75.7 | 39.4 | 42.5 | 46.4 | 152.4 | 155.6 | 173.4 |
| **Basaltic Bedrock Class** | | | | | | | | | | | | | |
| VT51 | Jeremys Run | 31 | 0 | 69 | 110.5 | 120.8 | 137.8 | 128.6 | 133.6 | 138.6 | 313.5 | 320.7 | 328.3 |
| PINE | Piney River | 0 | 31 | 69 | 138.3 | 145.1 | 159.3 | 68.3 | 71.8 | 76.2 | 278.8 | 296.4 | 307.8 |
| VT61 | North Fork Thornton River | 5 | 27 | 68 | 177.1 | 190.5 | 205.8 | 92.4 | 95.0 | 96.6 | 358.7 | 364.5 | 378.0 |
| VT66 | Rose River | 0 | 9 | 91 | 96.1 | 102.8 | 108.0 | 56.1 | 58.4 | 61.3 | 230.0 | 231.6 | 245.3 |
| VT75 | White Oak Canyon Run | 0 | 14 | 86 | 87.0 | 89.4 | 99.6 | 55.3 | 59.4 | 60.6 | 210.1 | 212.8 | 220.3 |

[a] The data cover 14 water years except for VT75 (11 years)

Table VI-1 c. Interquartile distributions of ANC, sulfate and sum of base cations (Ca+Mg+Na+K) for SHEN study streams during the period 1988 to 2001 for SPRING quarterly samples (sampled in the last week of April). [a]

| Site ID | Watershed | Percent of Watershed Area | | | ANC (ueq/L) | | | $SO_4$ (ueq/L) | | | SBC (ueq/L) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Siliciclastic | Granitic | Basaltic | 25th | median | 75th | 25th | median | 75th | 25th | median | 75th |
| **Siliciclastic Bedrock Class** | | | | | | | | | | | | | |
| DR01 | Deep Run | 100 | 0 | 0 | -0.4 | 0.3 | 1.2 | 101.1 | 103.8 | 107.7 | 129.8 | 131.1 | 132.4 |
| PAIN | Paine Run | 100 | 0 | 0 | 3.0 | 4.5 | 5.3 | 107.2 | 109.4 | 112.1 | 142.8 | 144.4 | 148.6 |
| VT36 | Meadow Run | 100 | 0 | 0 | -4.2 | -1.8 | -0.7 | 87.1 | 89.6 | 93.2 | 112.3 | 114.6 | 118.2 |
| VT53 | Twomile Run | 100 | 0 | 0 | 8.9 | 10.8 | 12.8 | 94.9 | 98.5 | 100.9 | 138.1 | 140.4 | 144.5 |
| WOR1 | White Oak Run | 100 | 0 | 0 | 15.1 | 19.0 | 23.3 | 72.5 | 77.8 | 81.6 | 131.0 | 139.8 | 145.0 |
| **Granitic Bedrock Class** | | | | | | | | | | | | | |
| NFDR | North Fork Dry Run | 0 | 100 | 0 | 44.8 | 48.3 | 51.0 | 93.3 | 97.5 | 101.8 | 201.5 | 211.7 | 216.0 |
| VT58 | Brokenback Run | 0 | 93 | 7 | 71.8 | 77.0 | 81.9 | 37.3 | 40.7 | 42.1 | 152.3 | 156.1 | 163.2 |
| STAN | Staunton River | 0 | 100 | 0 | 74.6 | 76.1 | 81.4 | 40.9 | 43.0 | 45.5 | 155.6 | 157.5 | 160.9 |
| VT62 | Hazel River | 0 | 100 | 0 | 79.5 | 87.3 | 91.8 | 35.5 | 37.1 | 38.6 | 162.4 | 167.8 | 174.6 |
| **Basaltic Bedrock Class** | | | | | | | | | | | | | |
| VT51 | Jeremys Run | 31 | 0 | 69 | 151.5 | 161.6 | 171.9 | 121.9 | 126.8 | 132.2 | 328.3 | 340.7 | 358.2 |
| PINE | Piney River | 0 | 31 | 69 | 187.4 | 198.0 | 207.2 | 61.0 | 64.2 | 69.1 | 318.4 | 324.4 | 341.7 |
| VT61 | North Fork Thornton River | 5 | 27 | 68 | 231.7 | 253.3 | 265.4 | 78.7 | 85.1 | 90.9 | 389.7 | 392.7 | 416.4 |
| VT66 | Rose River | 0 | 9 | 91 | 132.5 | 135.0 | 142.2 | 50.0 | 52.2 | 58.5 | 247.9 | 256.9 | 270.7 |
| VT75 | White Oak Canyon Run | 0 | 14 | 86 | 117.6 | 122.0 | 128.6 | 50.4 | 53.1 | 57.4 | 227.5 | 237.6 | 251.1 |

[a] The data cover 14 water years except for VT75 (11 years)

Table VI-1 d. Interquartile distributions of ANC, sulfate and sum of base cations (Ca+Mg+Na+K) for SHEN study streams during the period 1988 to 2001 for SUMMER quarterly samples (sampled in the last week of July). [a]

| Site ID | Watershed | Percent of Watershed Area | | | ANC (ueq/L) | | | $SO_4$ (ueq/L) | | | SBC (ueq/L) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Siliciclastic | Granitic | Basaltic | 25th | median | 75th | 25th | median | 75th | 25th | median | 75th |
| **Siliciclastic Bedrock Class** | | | | | | | | | | | | | |
| DR01 | Deep Run | 100 | 0 | 0 | 1.9 | 4.4 | 7.0 | 82.6 | 82.9 | 87.6 | 125.5 | 129.7 | 134.3 |
| PAIN | Paine Run | 100 | 0 | 0 | 7.4 | 10.4 | 12.0 | 102.7 | 104.7 | 110.4 | 147.7 | 151.2 | 157.4 |
| VT36 | Meadow Run | 100 | 0 | 0 | -4.3 | -1.6 | 0.1 | 72.8 | 74.9 | 81.0 | 107.1 | 108.3 | 111.3 |
| VT53 | Twomile Run | 100 | 0 | 0 | 19.9 | 23.0 | 25.4 | 75.1 | 83.8 | 88.1 | 137.0 | 140.6 | 147.8 |
| WOR1 | White Oak Run | 100 | 0 | 0 | 34.9 | 49.1 | 55.3 | 70.5 | 75.1 | 77.3 | 164.4 | 174.4 | 179.2 |
| **Granitic Bedrock Class** | | | | | | | | | | | | | |
| NFDR | North Fork Dry Run | 0 | 100 | 0 | 44.8 | 48.3 | 51.0 | 93.3 | 97.5 | 101.8 | 201.5 | 211.7 | 216.0 |
| VT58 | Brokenback Run | 0 | 93 | 7 | 71.8 | 77.0 | 81.9 | 37.3 | 40.7 | 42.1 | 152.3 | 156.1 | 163.2 |
| STAN | Staunton River | 0 | 100 | 0 | 74.6 | 76.1 | 81.4 | 40.9 | 43.0 | 45.5 | 155.6 | 157.5 | 160.9 |
| VT62 | Hazel River | 0 | 100 | 0 | 79.5 | 87.3 | 91.8 | 35.5 | 37.1 | 38.6 | 162.4 | 167.8 | 174.6 |
| **Basaltic Bedrock Class** | | | | | | | | | | | | | |
| VT51 | Jeremys Run | 31 | 0 | 69 | 248.2 | 277.0 | 347.2 | 90.3 | 94.5 | 103.4 | 399.8 | 414.5 | 483.5 |
| PINE | Piney River | 0 | 31 | 69 | 304.2 | 317.4 | 330.8 | 49.7 | 52.5 | 54.5 | 403.2 | 409.1 | 420.9 |
| VT61 | North Fork Thornton River | 5 | 27 | 68 | 358.7 | 386.0 | 411.0 | 57.9 | 63.4 | 68.6 | 472.4 | 488.8 | 505.4 |
| VT66 | Rose River | 0 | 9 | 91 | 179.0 | 188.6 | 205.0 | 41.1 | 46.9 | 53.2 | 294.0 | 299.2 | 312.0 |
| VT75 | White Oak Canyon Run | 0 | 14 | 86 | 168.2 | 177.8 | 198.6 | 42.2 | 49.8 | 52.7 | 273.6 | 286.3 | 313.0 |

[a] The data cover 14 water years except for VT75 (11 years)

Table VI-1 e. Interquartile distributions of ANC, sulfate and sum of base cations (Ca+Mg+Na+K) for SHEN study streams during the period 1988 to 2001 for FALL quarterly samples (sampled in the last week of October).[a]

| Site ID | Watershed | Percent of Watershed Area | | | ANC (ueq/L) | | | $SO_4$ (ueq/L) | | | SBC (ueq/L) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Siliciclastic | Granitic | Basaltic | 25th | median | 75th | 25th | median | 75th | 25th | median | 75th |
| **Siliciclastic Bedrock Class** | | | | | | | | | | | | | |
| DR01 | Deep Run | 100 | 0 | 0 | 2.8 | 4.5 | 6.2 | 88.0 | 94.6 | 104.0 | 129.5 | 133.3 | 137.5 |
| PAIN | Paine Run | 100 | 0 | 0 | 6.9 | 12.6 | 16.5 | 110.1 | 114.2 | 117.1 | 150.3 | 152.3 | 156.4 |
| VT36 | Meadow Run | 100 | 0 | 0 | -0.3 | 1.2 | 5.4 | 72.1 | 79.6 | 90.2 | 103.6 | 109.1 | 116.1 |
| VT53 | Twomile Run | 100 | 0 | 0 | 13.2 | 21.1 | 24.4 | 92.5 | 98.6 | 103.6 | 142.3 | 146.3 | 149.4 |
| WOR1 | White Oak Run | 100 | 0 | 0 | 24.7 | 34.5 | 50.0 | 77.8 | 81.0 | 83.1 | 142.7 | 159.6 | 179.1 |
| **Granitic Bedrock Class** | | | | | | | | | | | | | |
| NFDR | North Fork Dry Run | 0 | 100 | 0 | 59.3 | 73.2 | 87.8 | 94.2 | 98.1 | 101.2 | 221.5 | 226.0 | 246.5 |
| VT58 | Brokenback Run | 0 | 93 | 7 | 87.9 | 95.7 | 119.4 | 37.4 | 40.2 | 42.8 | 166.8 | 171.2 | 198.1 |
| STAN | Staunton River | 0 | 100 | 0 | 81.3 | 87.4 | 102.5 | 36.8 | 38.6 | 41.5 | 165.7 | 169.6 | 181.5 |
| VT62 | Hazel River | 0 | 100 | 0 | 97.4 | 106.6 | 131.1 | 33.0 | 35.9 | 39.0 | 173.9 | 190.0 | 208.5 |
| **Basaltic Bedrock Class** | | | | | | | | | | | | | |
| VT51 | Jeremys Run | 31 | 0 | 69 | 194.6 | 248.0 | 341.4 | 105.2 | 110.6 | 115.0 | 367.7 | 401.5 | 504.7 |
| PINE | Piney River | 0 | 31 | 69 | 214.2 | 244.2 | 281.9 | 53.7 | 59.8 | 63.1 | 336.6 | 357.0 | 383.0 |
| VT61 | North Fork Thornton River | 5 | 27 | 68 | 295.2 | 309.7 | 367.7 | 63.6 | 73.8 | 82.8 | 416.9 | 439.7 | 488.6 |
| VT66 | Rose River | 0 | 9 | 91 | 146.0 | 170.4 | 202.9 | 44.6 | 47.4 | 50.4 | 256.2 | 270.2 | 294.6 |
| VT75 | White Oak Canyon Run | 0 | 14 | 86 | 134.1 | 146.2 | 170.2 | 44.5 | 45.4 | 49.1 | 235.9 | 253.0 | 280.8 |

[a] The data cover 14 water years except for VT75 (11 years)

except those that had significant disturbance factors within the watersheds such as campgrounds, restaurants, visitor centers, waste-water treatment facilities, or roads subject to salt treatment. An additional small number of streams were not selected due to access problems.

The selection of long-term monitoring streams provided a reasonably unbiased representation of streams on the three major bedrock types in SHEN. As indicated in Table VI-2, the proportional representation of bedrock type by the primary SWAS study watersheds closely corresponded to the proportional distribution of bedrock types in SHEN. In addition, it has been shown that streamwater ANC distributions for the SWAS study watersheds, classified by predominant bedrock type, generally correspond to the distribution of observed ANC concentrations for the three major SHEN bedrock types (Webb et al. 1993, Galloway et al. 1999).

Table VI-2. Bedrock distribution in SHEN and SWAS watersheds.

| Site ID | Stream | Watershed Area ($km^2$) | Percent Bedrock Coverage[a] | | |
|---|---|---|---|---|---|
| | | | Siliciclastic | Granitic | Basaltic |
| VT51 | Jeremys Run | 22.0 | 31.0 | 0.0 | 69.0 |
| VT61 | North Fork Thornton River | 19.1 | 5.2 | 27.0 | 67.8 |
| VT60 | Piney River (PINE) | 12.4 | 0.0 | 31.3 | 68.7 |
| VT58 | Brokenback Run | 9.9 | 0.0 | 93.4 | 6.6 |
| VT62 | Hazel River | 13.2 | 0.0 | 100.0 | 0.0 |
| NFDR | North Fork Dry Run | 2.3 | 0.0 | 100.0 | 0.0 |
| VT66 | Rose River | 23.7 | 0.0 | 9.1 | 90.9 |
| VT59 | Staunton River (STAN) | 10.5 | 0.0 | 100.0 | 0.0 |
| VT75 | Whiteoak Canyon (Robinson River) | 14.1 | 0.0 | 14.1 | 85.9 |
| DR01 | Deep Run | 3.1 | 100.0 | 0.0 | 0.0 |
| VT36 | Meadow Run | 8.9 | 100.0 | 0.0 | 0.0 |
| VT35 | Paine Run (PAIN) | 12.4 | 100.0 | 0.0 | 0.0 |
| VT53 | Twomile Run | 5.6 | 100.0 | 0.0 | 0.0 |
| WOR1 | White Oak Run | 5.1 | 100.0 | 0.0 | 0.0 |
| Total SWAS Watersheds | | 162.3 | 26.4 | 29.8 | 43.7 |
| Total Shenandoah National Park | | 797.0 | 28.8 | 32.4 | 38.8 |

[a] percent of the watershed area underlain by bedrock within each of the major geologic sensitivity classes

Additional water quality data were collected in a spatially-intensive water chemistry survey conducted within 11 of the 14 primary SWAS study watersheds during March of 1992 in association with the Shenandoah National Park:Fish in Sensitive Habitats (FISH) project. The spatial distribution of measured streamwater ANC determined for all sites (n = 220) sampled in the 1992 survey is illustrated in Figure VI-2.

*a. Relationships between Geology and Streamwater Chemistry*

The SHEN landscape includes three major geologic sensitivity types: siliciclastic (quartzite and sandstone), granitic, and basaltic (Figure VI-1). Each of these bedrock types influences about one-third of the stream length in the park.

All of the primary SWAS streams on siliciclastic bedrock monitored during the period 1988 to 1999 had relatively high median $SO_4^{2-}$ concentration (76-109 μeq/L), whereas three of four streams monitored on granitic bedrock had $SO_4^{2-}$ concentration < 43 μeq/L. Sulfate concentrations in streams draining basaltic bedrock were more variable, ranging from 52 to 127 μeq/L. Streamwater base cation concentrations and ANC also varied dramatically from site to site. Median streamwater base cation concentrations were generally lowest in the watersheds on siliciclastic bedrock, and this could reflect lower base cation supply from watershed soils and/or greater base cation depletion of soils caused by leaching of $SO_4^{2-}$ to streams. Base cation concentrations were substantially higher (median > 235 μeq/L) in watersheds on basaltic bedrock.

There are many streams on siliciclastic bedrock in the park that have chronic ANC in the range where adverse effects are likely to occur on sensitive aquatic biota and where episodic acidification to ANC values near or below zero frequently occur during hydrological events. The streams that are most susceptible to adverse chronic or episodic effects on in-stream biota are those having chronic ANC less than about 50 μeq/L, especially those having chronic ANC less than about 20 μeq/L. These are also primarily on siliciclastic bedrock (Table VI-1).

The observed patterns in streamwater chemistry are strongly related to patterns in bedrock geology within the park (Figure VI-1). In fact, geological type, soils conditions that developed from underlying geology, and water chemistry conditions are all closely interrelated within SHEN. This is partly because rock and soils materials in SHEN and elsewhere in the Southeast were not transported from place to place (and thereby mixed) by the process of glaciation.

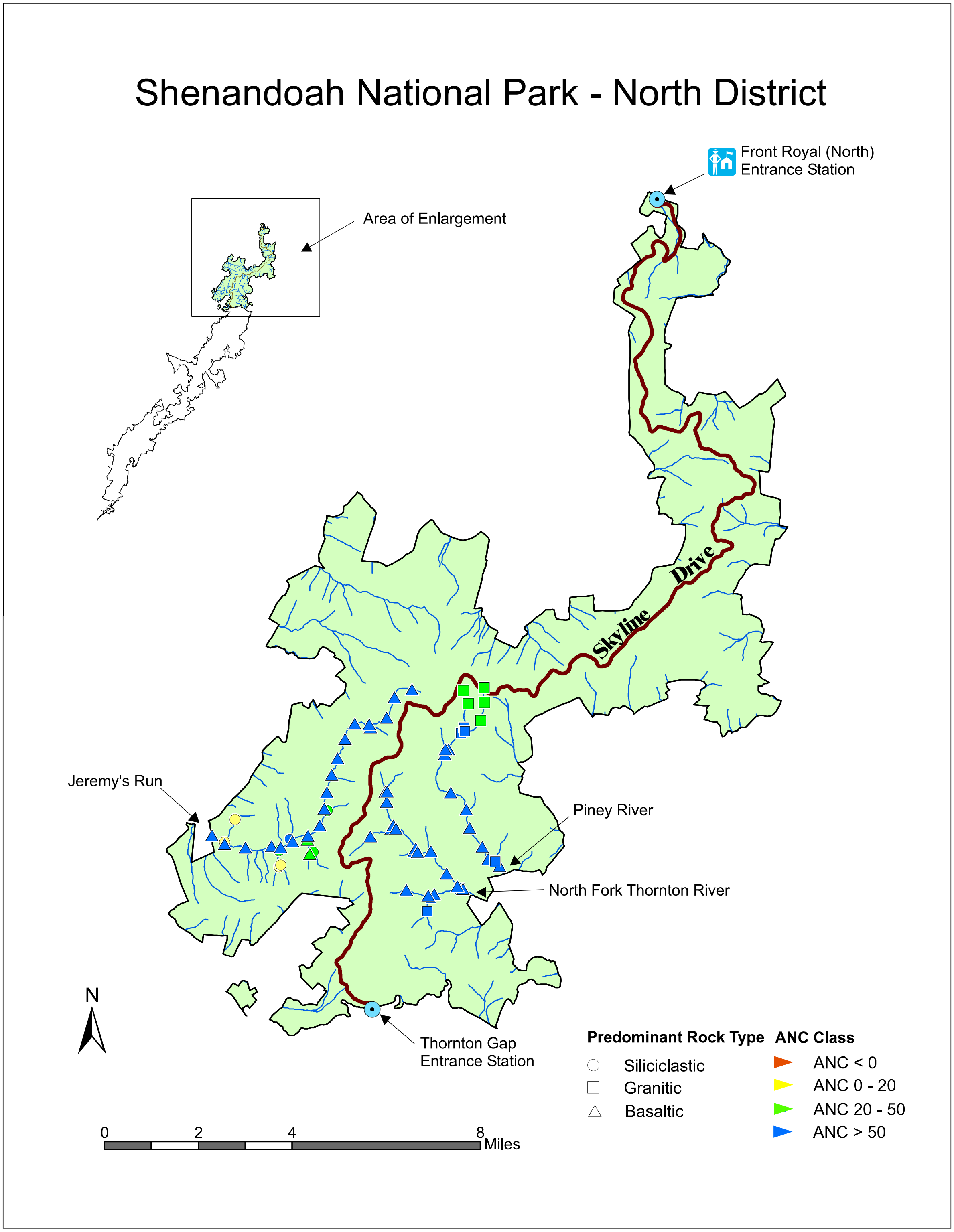



Figure VI-2. Distribution of streamwater ANC determined in the 1992 spring survey of water chemistry within 11 watersheds in SHEN. Stream sampling sites are coded according to ANC class (colors) and geologic sensitivity class (symbol shape).

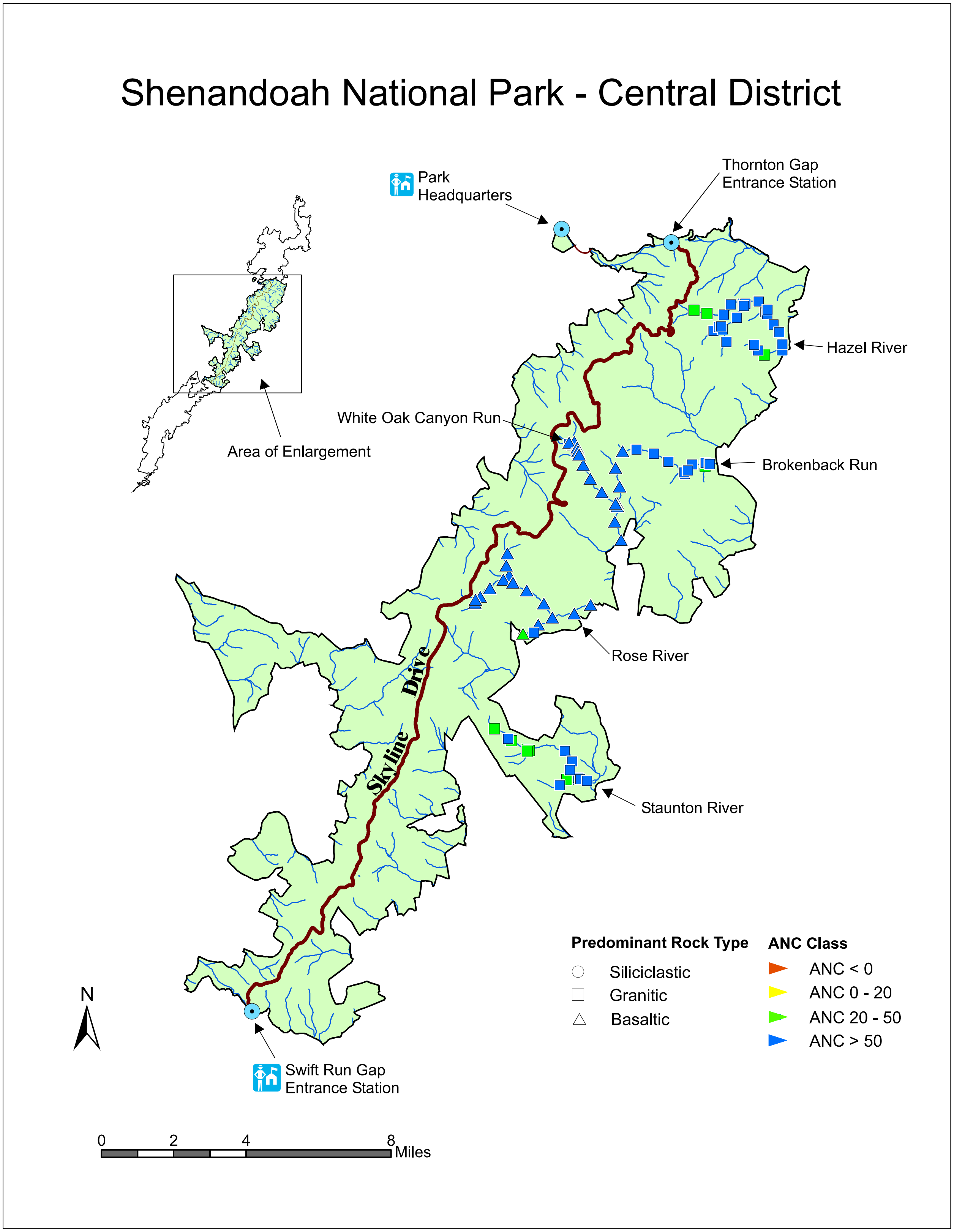



Figure VI-2. Continued.

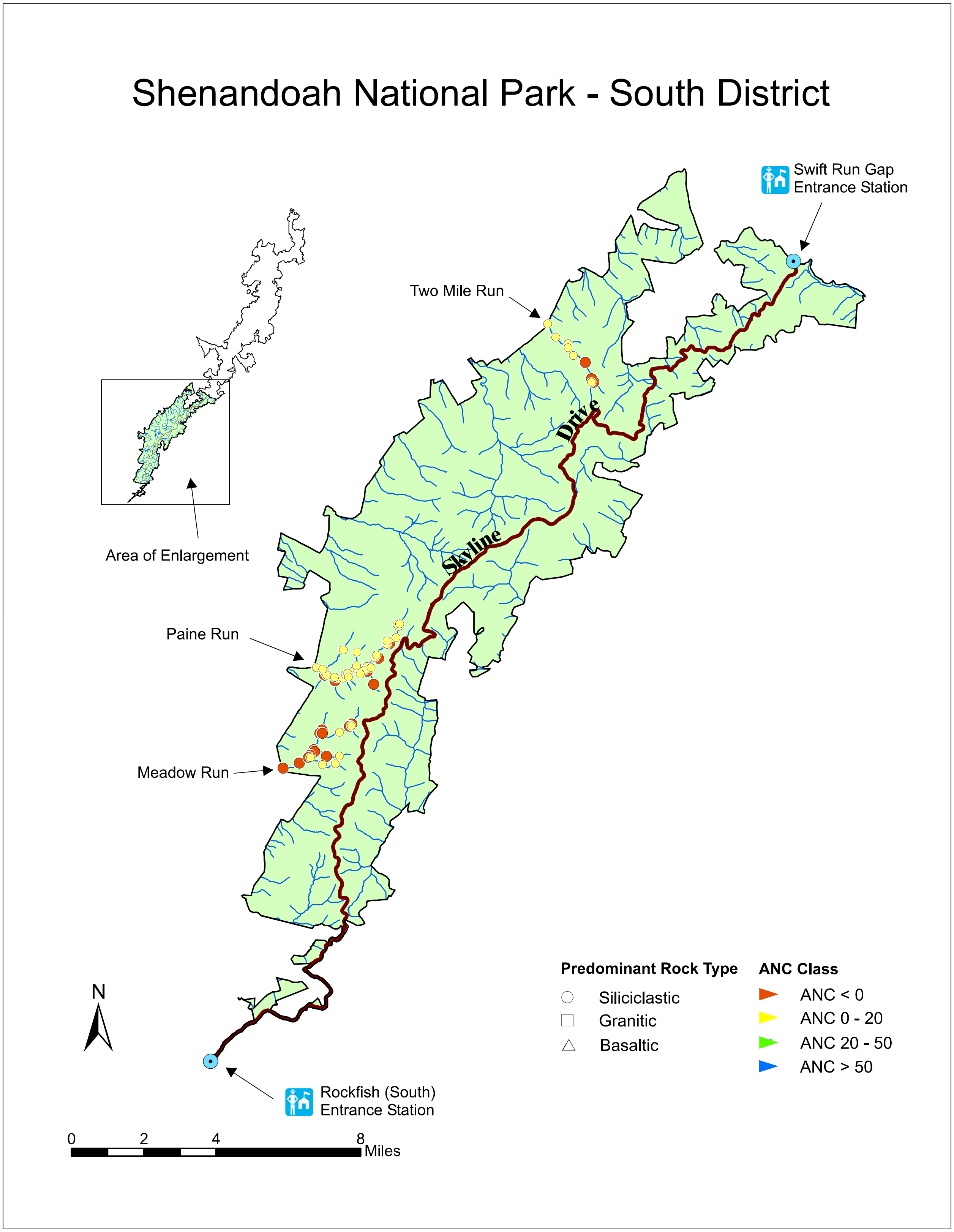



Figure VI-2. Continued.

Relationships between water chemistry and geology within SHEN have been known for some time. Lynch and Dise (1985) reported results from six synoptic surveys of 56 streams that drain SHEN. Concentrations of silica, base cations, and ANC were strongly related to the distribution of geologic formations. The effects of acidification were often greatest in watersheds underlain by the Antietam Formation (Figure II-4), which had streamwater pH averaging 5.0 and ANC averaging -7 μeq/L. Lynch and Dise (1985) found that flow-weighted streamwater ANC decreased in order of the underlying geologic formation as follows:

> basaltic (Catoctin formation) > granitic (Pedlar and Old Rag formations) > siliciclastic (Hampton and Antietam formations)

Regression relationships suggested that streamwater ANC would generally range from about 175 μeq/L on the Catoctin Formation to -7 μeq/L on the Antietam Formation. After accounting for variations in streamwater chemistry with geology, Lynch and Dise (1985) further found lower streamwater ANC on the western side of the park, as compared with the eastern side. The authors speculated that this could be due to the upwind sources of acidic deposition being in closer proximity to the park's western border, which results in greater S deposition on west-facing slopes. However, there are also soils differences between east- and west-facing slopes (Figures II-5 and VI-2), which might be important.

Additional perspective concerning the relationship between streamwater chemistry and geology in SHEN is provided by the 1992 survey of sub-watersheds within the primary study watersheds. Whereas Lynch and Dise (1985) derived regression models to predict streamwater composition as function of multiple bedrock types, the 1992 survey provides an opportunity to examine the composition of streamwaters associated with single bedrock types. From the relatively large number of small watersheds sampled in the survey, subsets of 62 siliciclastic, 46 granitic, and 15 basaltic subwatersheds were identified. Table VI-3 presents descriptive statistics for measurements of ANC, pH, sum of base cations, and $SO_4^{2-}$ concentrations obtained for the subset of the 1992 survey samples (n = 123) associated with single bedrock types. The bedrock-related differences in ANC and pH distributions are consistent with expectations based on the earlier Lynch and Dise (1985) analysis.

As indicated in Table VI-3, streamwater ANC and pH values were lowest for the surveyed siliciclastic subwatersheds and highest for basaltic subwatersheds. Almost half of the sampled streams in siliciclastic subwatersheds had ANC in the chronically acidic range (< 0 μeq/L) in

Table VI-3. Range and distribution of streamwater concentrations within SHEN associated with major bedrock classes: Spring 1992 Synoptic Survey (Galloway et al. 1999).

| | n | Minimum | 25% | Median | 75% | Maximum |
|---|---|---|---|---|---|---|
| **ANC (μeq/L)** | | | | | | |
| Siliciclastic | 62 | -18.1 | -1.0 | 1.2 | 3.7 | 12.8 |
| Granitic | 46 | 22.0 | 47.2 | 58.7 | 67.0 | 130.4 |
| Basaltic | 15 | 33.7 | 97.0 | 149.2 | 179.0 | 226.7 |
| **pH** | | | | | | |
| Siliciclastic | 62 | 4.8 | 5.4 | 5.6 | 5.7 | 6.0 |
| Granitic | 46 | 6.0 | 6.7 | 6.8 | 6.8 | 7.1 |
| Basaltic | 15 | 6.6 | 6.9 | 7.1 | 7.2 | 7.3 |
| **Sum of Base Cations (μeq/L)** | | | | | | |
| Siliciclastic | 62 | 92.1 | 138.1 | 168.2 | 190.4 | 272.1 |
| Granitic | 46 | 89.5 | 136.7 | 147.7 | 161.3 | 243.5 |
| Basaltic | 15 | 138.0 | 232.0 | 369.5 | 381.1 | 450.9 |
| **Sulfate (μeq/L)** | | | | | | |
| Siliciclastic | 62 | 67.2 | 88.5 | 97.2 | 104.8 | 177.8 |
| Granitic | 46 | 13.4 | 30.1 | 36.6 | 42.1 | 96.3 |
| Basaltic | 15 | 12.3 | 36.2 | 62.2 | 97.9 | 164.3 |

Notes: (1) The data were obtained for watersheds underlain by a single bedrock type.
(2) 25% and 75% refer to the 25th and 75th percentile values. 50 percent of all the values are within the interquartile range, as bounded by the 25th and 75th percentile values.

which lethal effects on brook trout are probable (see Section VI.B.3). The balance of the streams associated with siliciclastic bedrock had ANC in the episodically acidic range (having chronic ANC in the range 0-20 μeq/L) in which sub-lethal or lethal effects are possible. Many of the streams associated with the granitic bedrock type were in the indeterminate range (20-50 μeq/L). In contrast, the streams associated with the basaltic bedrock type had ANC values that were well within the suitable range for brook trout.

The pH values for the streams in the 1992 survey displayed a similar relationship with bedrock type, with the streams having lowest pH being associated with siliciclastic bedrock and those having highest pH associated with basaltic bedrock. All of the streams on siliciclastic bedrock had pH < 6, identified by Baker and Christiansen (1991) as too acidic for some acid-sensitive fish species.

Sulfate concentration values for streams in the 1992 survey also differed among bedrock types. This difference is critically important with respect to the observed streamwater ANC, which is determined by the relative concentrations of base cations and acid anions. Whereas both the siliciclastic and basaltic bedrock types were associated with relatively high streamwater $SO_4^{2-}$ concentrations, the siliciclastic bedrock type was associated with much lower base cation concentrations, and therefore lower streamwater ANC. In contrast, streams on granitic bedrock exhibited both low base cation and low $SO_4^{2-}$ concentrations, with resulting intermediate ANC.

The observed differences in streamwater $SO_4^{2-}$ concentrations for the major bedrock types in SHEN primarily reflect differences in $SO_4^{2-}$ retention properties of the associated soils. Watersheds in the southeastern United States commonly retain more than 50% of deposited S (Rochelle and Church 1987, Turner et al. 1990). This S retention is attributed to $SO_4^{2-}$ adsorption in the old and highly-weathered southeastern soils (Galloway et al. 1983, Baker et al. 1991). Although there are other mechanisms of S retention or immobilization in watersheds, including S reduction and biological uptake, these are generally considered less important on regional or park-specific scales than is adsorption, particularly in upland forests (Turner et al. 1990). Regardless of mechanism, S retention in watersheds reduces the potential for the acidification of surface waters that is associated with increasing concentrations and mobility of $SO_4^{2-}$. However, S retention by adsorption is a capacity-limited process. As the finite adsorption capacity of watershed soils is exhausted, $SO_4^{2-}$ concentrations can increase in surface waters, potentially contributing to greater acidification (Johnson and Cole 1980, Munson and Gherini 1991, Church et al. 1992). Moreover, as indicated by the available soil and water quality data for SHEN, there can be substantial variation in S retention capacity among watersheds in close geographic proximity.

Figure VI-3 illustrates the effect of varying S retention capacity on the estimated historic increase in $SO_4^{2-}$ concentrations in SHEN streamwaters. Median $SO_4^{2-}$ concentrations in 1992 are shown for streams on the major bedrock types in SHEN (Table VI-3) in relation to estimated background $SO_4^{2-}$ concentrations for low-ANC surface waters in the eastern United States (Brakke et al. 1989, Cosby et al. 1991). Whereas streamwater $SO_4^{2-}$ concentrations have increased by a factor of about 4.4 in streams on siliciclastic bedrock, $SO_4^{2-}$ concentrations have only increased by a factor of about 1.7 in streams on granitic bedrock. These differences are consistent with direct measurements of adsorption properties obtained by Webb (1988) and Ingersol (1994) for SHEN soils.

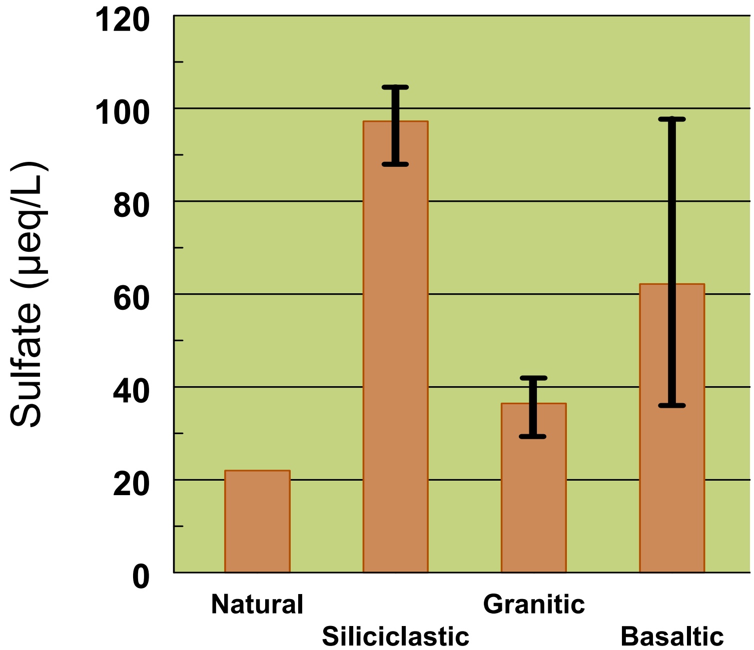



Figure VI-3. Comparison of estimated natural background and current median sulfate concentrations among streams located on major bedrock types in SHEN. Error bars delimit interquartile ranges for current conditions. (Current concentrations based on 1992 survey data; see Table VI-3.)

Comparison of current median streamwater $SO_4^{2-}$ concentrations with steady-state concentration values calculated from current precipitation, evapotranspiration, and deposition provides an estimate of percent S retention values. Based on estimated deposition and runoff values for 1990, the average steady-state $SO_4^{2-}$ concentration for streamwaters in SHEN was 120 µeq/L. Comparison of this value with the median $SO_4^{2-}$ concentration values in Table VI-3 provides S retention estimates for siliciclastic watersheds of 19%, for granitic watersheds of 70%, and for basaltic watersheds of 49%. Given the resulting effect of $SO_4^{2-}$ leaching on streamwater ANC, this is a difference with significant geochemical and biological implications.

*b. Relationships between Soils and Streamwater Chemistry*

A common measure of base availability in soils is the percent base saturation, which represents the fraction of exchange sites (or cation exchange capacity [CEC]) occupied by base cations. Base saturation values in the range of 10–20% have been cited as threshold values for incomplete acid neutralization and leaching of aluminum (Al) from soil to surface waters (Reuss and Johnson 1986, Binkley et al. 1989, Cronan and Schofield 1990). Data from the 2000 soil survey conducted by the University of Virginia (Welsch et al. 2001) are summarized in Table VI-4 for each of the study watersheds, stratified by the predominant bedrock class present in each watershed. As indicated in Figure VI-4, median base saturation was generally less than 10% for mineral soils associated with siliciclastic bedrock and less than about 14% for mineral soils associated with granitic bedrock in the park. The present low base cation availability in soils of watersheds underlain by siliciclastic or granitic bedrock is probably due to a combination of low base cation content of the parent bedrock and depletion by previous land use and decades of accelerated leaching by acidic deposition. The relative importance of these factors is not known. This low base cation availability suggests the potential for leaching of Al to streams.

Table VI-4. Interquartile distribution of pH, cation exchange capacity (CEC), and percent base saturation for soil samples[a] collected in SHEN study watersheds during the 2000 soil survey.

| Site ID | Watershed | n | pH | | | CEC (cmol/kg) | | | Percent Base Saturation | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 25th | Med | 75th | 25th | Med | 75th | 25th | Med | 75th |
| **Siliciclastic Bedrock Class[b]** | | | | | | | | | | | |
| PAIN | Paine Run | 6 | 4.4 | 4.5 | 4.7 | 3.7 | 5.7 | 5.7 | 7.1 | 10.0 | 24.9 |
| WOR1 | White Oak Run | 6 | 4.3 | 4.4 | 4.4 | 4.8 | 7.5 | 7.8 | 5.3 | 7.5 | 8.5 |
| DR01 | Deep Run | 5 | 4.3 | 4.4 | 4.5 | 3.9 | 5.0 | 5.8 | 7.2 | 8.9 | 10.8 |
| VT36 | Meadow Run | 6 | 4.4 | 4.4 | 4.5 | 3.1 | 3.5 | 7.6 | 7.8 | 8.7 | 11.3 |
| VT53 | Twomile Run | 5 | 4.3 | 4.5 | 4.5 | 4.6 | 6.0 | 6.9 | 11.7 | 12.3 | 13.6 |
| **Granitic Bedrock Class** | | | | | | | | | | | |
| STAN | Staunton River | 6 | 4.7 | 4.8 | 4.9 | 6.5 | 7.5 | 9.2 | 9.1 | 13.9 | 29.5 |
| NFDR | NF of Dry Run | 5 | 4.4 | 4.5 | 4.7 | 7.3 | 8.0 | 9.2 | 7.5 | 10.8 | 12.4 |
| VT58 | Brokenback Run | 5 | 4.6 | 4.7 | 4.7 | 7.3 | 8.4 | 9.6 | 6.0 | 6.7 | 9.7 |
| VT62 | Hazel River | 4 | 4.5 | 4.7 | 4.8 | 5.3 | 5.3 | 6.5 | 12.3 | 12.8 | 21.6 |
| **Basaltic Bedrock Class** | | | | | | | | | | | |
| PINE | Piney River | 6 | 4.7 | 5.0 | 5.3 | 7.3 | 7.7 | 10.0 | 17.0 | 24.0 | 57.0 |
| VT66 | Rose River | 8 | 4.8 | 5.0 | 5.3 | 7.3 | 10.1 | 10.7 | 19.1 | 38.0 | 63.5 |
| VT75 | White Oak Canyon | 6 | 4.9 | 5.1 | 5.5 | 7.1 | 7.5 | 9.3 | 15.6 | 32.8 | 43.4 |
| VT61 | NF of Thornton River | 7 | 5.1 | 5.2 | 5.3 | 7.7 | 9.6 | 10.8 | 35.6 | 54.4 | 71.2 |
| VT51 | Jeremys Run | 4 | 4.7 | 5.0 | 5.3 | 6.3 | 7.6 | 7.7 | 15.0 | 22.8 | 46.1 |

[a] Samples collected from mineral soil >20cm depth
[b] Watersheds are stratified according to the predominant bedrock class present in each watershed.

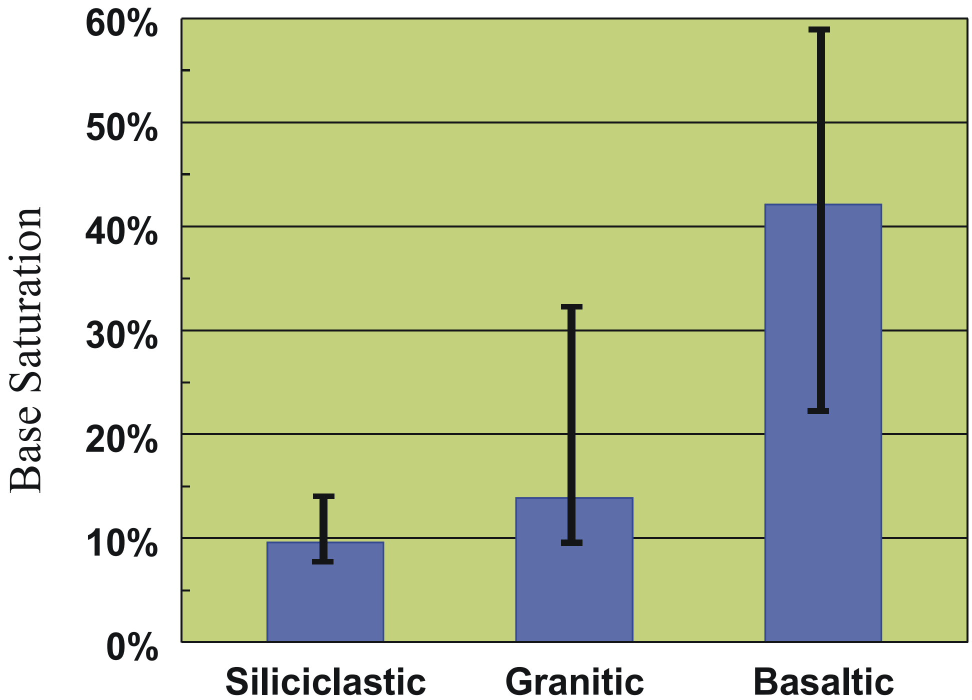



Figure VI-4. Median percent base saturation for soils associated with SHEN's three bedrock types. Brackets delimit interquartile ranges. The base saturation of soils derived from siliciclastic and granitic bedrock is too low for effective buffering of acidic deposition in many watersheds. The data were obtained for mineral-horizon soil samples collected in the summer of 2000 at 79 geologically distributed sites in SHEN (Welsch et al. 2001).

A clear relationship was found between streamwater ANC and measured soil base saturation among the SWAS watersheds (Figure VI-5). All watersheds that were characterized by soil base saturation less than 15% had average streamwater ANC < 100 µeq/L. Watersheds that had higher soil base saturation (all of which were > 22%) were dominated by the basaltic bedrock type and had average streamwater ANC > 100 µeq/L. Lowest base saturation values (7 to 14%) were found in the siliciclastic and granitic watersheds, with much higher values in the basaltic watersheds. We do not advocate using the relationship between streamwater ANC and soil base saturation, shown in Figure VI-5, for predictive purposes, however. Within a particular bedrock class, soil base saturation is not a good predictor of streamwater ANC. In addition, the ranges of base saturation among the study watersheds were similar for the siliciclastic and granitic types, despite the clear separation in streamwater ANC (Figure VI-5).

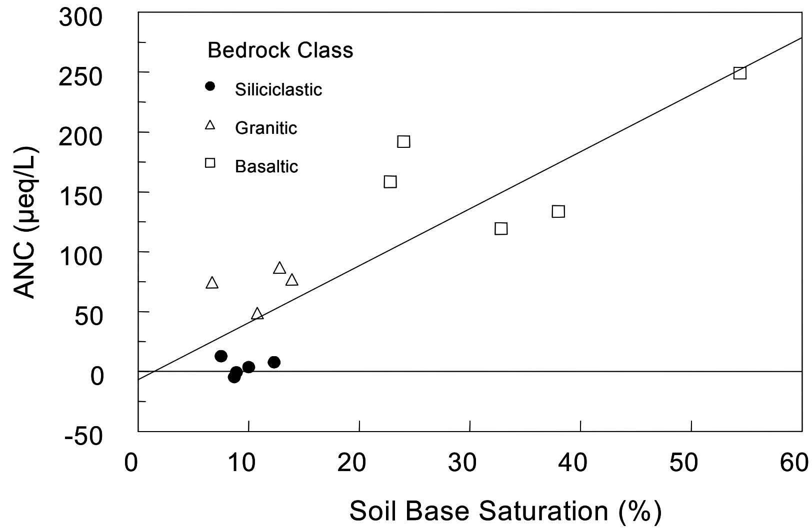



Figure VI-5. Median spring ANC of streams in SWAS watersheds during the period 1988 to 1999 versus median base saturation of watershed soils. Soils data were collected by the University of Virginia during the summer of 2000 (Welsch et al. 2001).

The data presented in Table VI-4 are based on soils data stratified by watershed, and each watershed was geologically classified based on the predominant bedrock type found within the watershed. However, a watershed that was primarily underlain by granitic bedrock may have included, for example, one or more soil pits located over basaltic bedrock. We therefore reanalyzed the soils data by classifying all soil pits according to the underlying bedrock type, irrespective of the predominant bedrock class within the watershed in which the soil pit was located. The results of this analysis, shown in Table VI-5, illustrate a more distinct separation of soils characteristics across bedrock types, especially for the mineral soil layer (> 20 cm depth). For example, the interquartile ranges ($25^{th}$ to $75^{th}$ percentile) for base saturation in the mineral soil were 8 to 14%, 10 to 32%, and 22 to 59% for the siliciclastic, granitic, and basaltic classes, respectively. Soil pH showed almost a complete interquartile separation, with interquartile ranges in the mineral soil of 4.4 to 4.6, 4.7 to 5.0, and 4.9 to 5.3 for the three respective bedrock types. Cation exchange capacity values were lower in the siliciclastic soils (interquartile range in the mineral soil of 3.7 to 7.5) than in the other two bedrock types, which showed similar CEC values (Table VI-5).

Table VI-5. Interquartile distributions for each bedrock class of pH, cation exchange capacity (CEC), and percent base saturation for all soil pits excavated within the 2000 soil survey.

| Bedrock Class and Soil Layer[a] | N | pH | | | CEC (cmol/kg) | | | Percent Base Saturation | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 25th | Med | 75th | 25th | Med | 75th | 25th | Med | 75th |
| **Siliciclastic Bedrock Class** | | | | | | | | | | |
| Surface soil | 28 | 4.1 | 4.2 | 4.4 | 6.9 | 10.5 | 13.5 | 9.9 | 15.3 | 28.3 |
| Mineral soil | 28 | 4.4 | 4.5 | 4.6 | 3.7 | 5.7 | 7.5 | 7.5 | 9.6 | 13.7 |
| **Granitic Bedrock Class** | | | | | | | | | | |
| Surface soil | 26 | 4.3 | 4.6 | 4.9 | 6.9 | 10.1 | 13.2 | 17.2 | 31.1 | 46.0 |
| Mineral soil | 26 | 4.7 | 4.8 | 5.0 | 6.9 | 8.1 | 10.5 | 10.1 | 13.9 | 32.3 |
| **Basaltic Bedrock Class** | | | | | | | | | | |
| Surface soil | 25 | 4.7 | 5.3 | 5.6 | 9.5 | 10.3 | 15.1 | 29.0 | 46.6 | 74.5 |
| Mineral soil | 25 | 4.9 | 5.1 | 5.3 | 7.4 | 8.1 | 10.1 | 22.0 | 42.1 | 58.8 |

[a] Surface soil collected from depth ≤20 cm; mineral soil collected from depth >20 cm. Each soil pit was classified into a bedrock class based on the location of the soil pit, irrespective of the predominant bedrock class within the watershed in which the soil pit was located.

c. *Influence of Forest Defoliation on Streamwater Chemistry*

Between the mid-1980s and the early 1990s, the southward expanding range of the European gypsy moth traversed SHEN and affected all of the SWAS study watersheds (Webb 1999). Some areas of the park were heavily defoliated two to three years in a row. The White Oak Run watershed, for example, was more than 90% defoliated in both 1991 and 1992. The gypsy moth population in White Oak Run then collapsed due to pathogen outbreak and there was no further heavy defoliation in subsequent years. This insect infestation of forest ecosystems in SHEN resulted in substantial impacts on streamwater chemistry. The most notable effects of the defoliation on park streams were dramatic increases in the concentration and export of N and base cations in streamwater. Figure VI-6 shows the increase in $NO_3^-$ export that occurred in White Oak Run. Following defoliation, $NO_3^-$ export increased to previously unobserved levels and remained high for over six years before returning to predefoliation levels. Eshleman et al. (2001) estimated that park-wide export of $NO_3^-$ in 1992, the year of peak defoliation, increased 1700% from a predefoliation baseline of about 0.1 kg/ha/yr. The very low levels of $NO_3^-$ export in park streams were consistent with expectations for N-limited, regenerating forests (e.g., Aber et al. 1989, Stoddard 1994). Release of $NO_3^-$ to surface waters following defoliation was

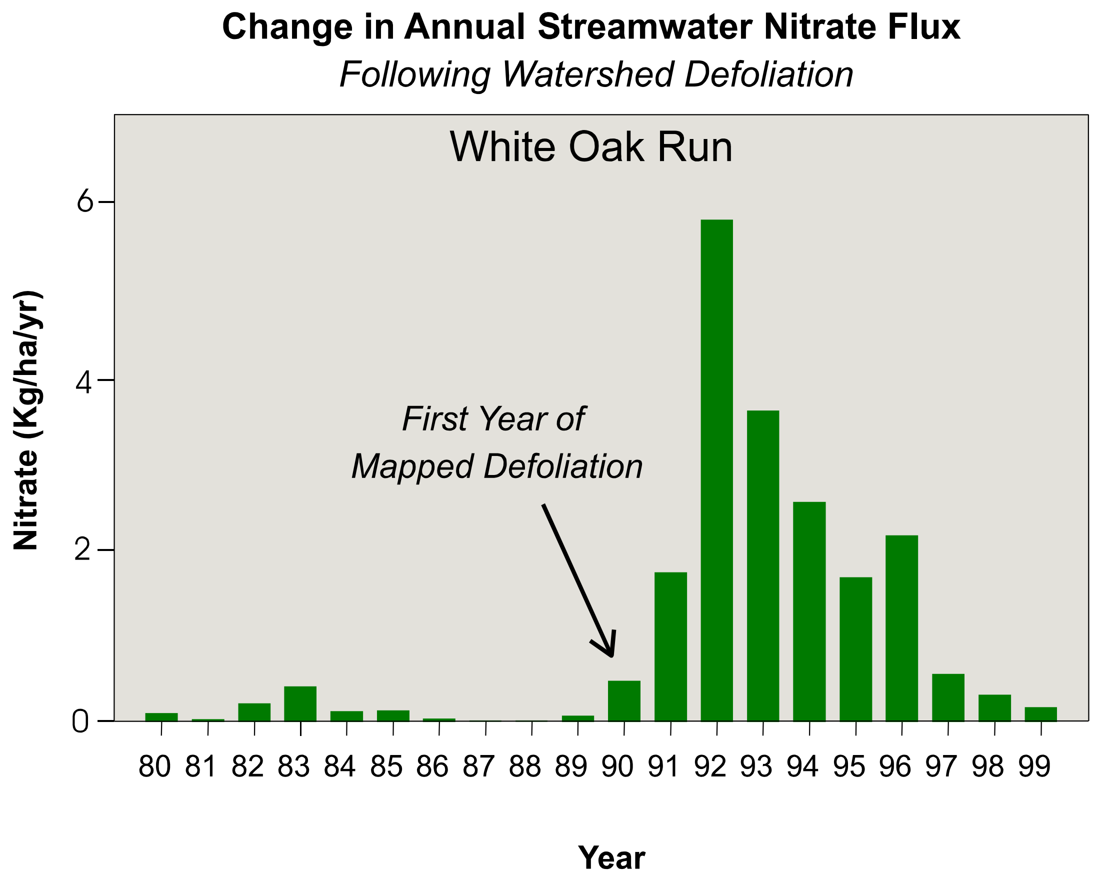



Figure VI-6. Effect of watershed defoliation by the gypsy moth caterpillar on nitrate flux in streamwater. White Oak Run was heavily defoliated for three consecutive years. The watershed area defoliated was 46.5% in 1990, 92.9% in 1991, and 90.4% in 1992. In 1993, the gypsy moth population collapsed and there was no further defoliation.

likewise consistent with previous observations of increased N export due to forest disturbance (e.g., Likens et al. 1970, Swank 1988). The exact mechanisms have not been determined, but it is evident that the repeated consumption and processing of foliage by the gypsy moth larva disrupted the ordinarily tight cycling of N in SHEN forests.

Although N is thought to play an important role in the chronic acidification of surface waters in some areas (c.f., Sullivan et al. 1997), the elevated concentrations of $NO_3^-$ in SHEN streams following defoliation did not appear to contribute to baseflow acidification in White Oak Run. This was due to a concurrent increase in concentrations of base cations in streamwater (Webb et al. 1995). Both $NO_3^-$ and base cation concentrations increased during high-runoff conditions, although the increase in base cations did not fully compensate for the episodic increase in $NO_3^-$. Episodic acidification following defoliation thus became more frequent and more extreme in terms of observed minimum ANC (Webb et al. 1995).

The full effect of the gypsy moth on aquatic resources in SHEN is not well understood. One consequence may be a reduction in the supply of available soil base cations and associated effects on streamwater ANC. Repeated periods of defoliation would probably increase the impact of episodic acidification on sensitive aquatic fauna and may determine the conditions under which some species are lost. Ultimately such effects may depend upon both the severity of future gypsy moth or other insect outbreaks and possibly on the amount of atmospheric N deposition. Gypsy moth populations typically display a pattern of periodic outbreaks and collapse (Cambell 1981). It remains to be seen what the long-term pattern will be.

*d. Regional Context*

In a regional context, SHEN is a major focal point of aquatic effects of S deposition, due largely to the prevalence of siliciclastic bedrock geology. Based on the two extensive probability sampling programs for streamwater chemistry within the region (National Stream Survey [NSS, Herlihy et al. 1993] and Environmental Monitoring and Assessment Program [EMAP, Herlihy et al. 2000]), there are about 11,300 km of wadeable stream in western Virginia. Data collected in EMAP showed about 10% of this stream length with ANC $\leq$ 50 μeq/L, and 5% with ANC $\leq$ 20 μeq/L. Many of these low-ANC streams are located in and around SHEN. The median value of streamwater ANC within the SAMI region was 172 μeq/L, based on an extrapolation of data from 154 NSS upstream reach sample sites to a population of 19,940 streams (Sullivan et al. 2002a). In contrast, the median ANC for 47 streams within SHEN was 82 μeq/L (Herlihy et al. 1996).

## 2. Trends in Streamwater Chemistry

Although SHEN has the longest continuous record of streamwater composition in a national park and among the longest anywhere in the United States, the record only goes back to 1979. The 14 SWAS streams that are located in the park (Figure VI-1) have quarterly water quality data extending back to 1988. These streams are used here to examine the trends in streamwater chemistry in the park over the period 1988 to 2001 (data actually cover the 14 water years from Oct. 1987 to Sept. 2001). Trends within the park are placed in a regional context by comparing results with trends calculated for the 65 VTSSS long-term monitoring streams which cover the western part of Virginia. The VTSSS trends are also based on quarterly streamwater samples, which were taken contemporaneously with the SWAS stream samples.

*a. Methods and Data*

Trends were calculated for individual ions in streamwater using all quarterly samples for all 14 years of the data record using two techniques: 1) simple linear regressions (SLR) of changes in ionic concentration over time; and 2) the seasonal Kendal tau test (SKT; Hirsch et al. 1982, Hirsch and Slack 1984), a commonly applied nonparametric test for monotonic trends in seasonally-varying water quality data. The slope estimates from the SKT and the SLR were compared and found to be essentially the same for all solutes and streams analyzed (Appendix E). In the discussion that follows, all trends are derived from the slope of the SLR technique and are in units of ueq/L/year, unless otherwise specified. Significance of trends, where expressed, are based on statistically significant deviations of the regression slope from a value of zero (the standard test of significance in simple linear regression analyses).

The 14 SWAS streams and 65 VTSSS streams cover a range of bedrock geology and occur within two physiographic provinces in western Virginia. This allows examination of the patterns of trends on different parts of the landscape. The quarterly nature of the data allows examination of seasonal trends in solute concentrations by performing the SLR analyses separately on winter, spring, summer and fall quarter samples. In these seasonal analyses, there will be 14 data points in the regressions as opposed to 56 data points (4x14) in the regression analyses when all quarters are used for annual trend estimation. Time series plots of the quarterly data for all solutes for the 14 SWAS streams, along with the SLR regression line, are presented in Appendix E.

Given that trend estimates are available for a number of streams in the park (or in western Virginia, or on a particular bedrock type, or in a particular physiographic province), it is sometimes useful to have a single measure of streamwater solute behavior for a region or group of streams. In such cases, the median value of the trend estimates for a solute for all streams within a group is used. The use of the median trend to summarize the regional response is common. For instance, median trends were used in the most recent EPA report to Congress concerning surface water responses to acidic deposition (Stoddard et al. 2003). The statistical significance of regional trends as represented by the median of a population of trend estimates is determined by calculating confidence limits about the median value in the distribution of all slopes in the analysis (SAS Institute Inc. 1988; Altman et al. 2000). Plots of the full distributions of annual trends for all solutes for all of the 65 VTSSS streams and all of the 14 SHEN streams are provided in Appendix E for comparison with the medians used in the discussions below.

*b. Results*

The utility of using the median trend for the 14 monitored streams in the park can be illustrated by examining the individual trends for all streams for a given solute (Figure VI-7). For example, ANC increased during the period of record at most streams, whereas $SO_4^{2-}$ and $NO_3^-$ concentrations generally decreased. Using the median provides a summary of the direction and magnitude of change in the population of streams. It is important to note that for a given solute and group of streams all trends may be in the same direction and of the same magnitude as the median trend. However, it is frequently the case that the magnitudes and even the directions of trends in some streams may be very different from the medians. An examination of plots for all of the ranked slope distributions for all solutes, partitioned by season, physiography or lithology, would be at best tedious and at worst confusing. In order to elucidate and understand the general patterns in the trends of streamwater chemistry, and their relationship to season and to the landscape, the median slope values (median trends) for each solute will be used to discuss the patterns in trends in streamwater chemistry in SHEN.

The median trends for each solute in the 14 SWAS streams are summarized in Table VI-6 along with the median trends for the 65 VTSSS streams for the same solutes and period. Note that the 14 SWAS streams are also included in the analyses of the 65 VTSSS streams. Median trends were also calculated for the basic streamwater chemistry data disaggregated by season and physiographic province or bedrock geology (Table VI-6).

The general trends in streamwater chemistry in the park can be understood by considering the behavior of $SO_4^{2-}$, the sum of the base cations (SBC = Ca + Mg + Na + K), and ANC. Median annual and seasonal trends for ANC, $SO_4^{2-}$, and SBC determined for streams within geographically and lithologically defined classes are displayed in Figures VI-8 through VI-10. These median trends are extracted from Table VI-6 and presented graphically to aid discussion. The significance of any of the trends in the figures can be determined by reference to Table VI-

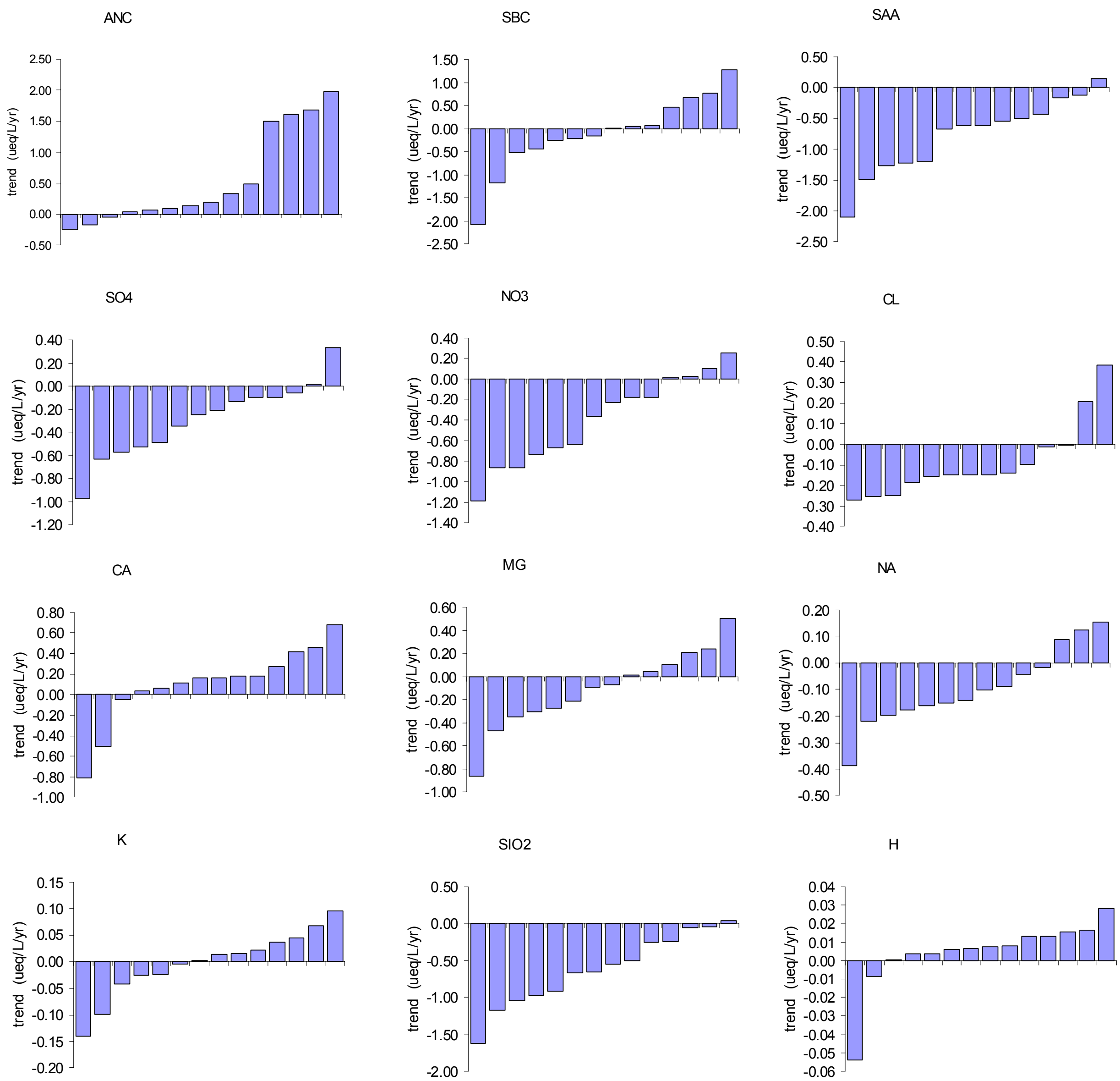



Figure VI-7. Trends in solute concentrations for the 14 SWAS streams in SHEN (ueq/L/yr). The trends are the slopes of simple linear regressions on all quarterly data for 14 years (1988 to 2001; n=56). For each solute, the trends have been sorted from lowest to highest to display the range of estimated trends in a given solute across the 14 streams. Each bar represents one stream.

Table VI-6. Median trends in solute concentrations within geographically or lithologically defined classes for the 14-year period 1988-2001 (water years). The median trends were derived from the slopes of simple linear regressions on all quarterly data for annual trends (n=56), or on individual quarterly values for seasonal trends (n=14). Significant trends ($p < .05$) are indicated in bold.

| Sites | N sites | Annual Trends | Seasonal Trends | | | |
|---|---|---|---|---|---|---|
| | | | Winter | Spring | Summer | Fall |
| **ANC (µeq/L)** | | | | | | |
| All Virginia Sites | 65 | -0.015 | -0.138 | -0.015 | 0.084 | 0.287 |
| Blue Ridge Sites | 37 | 0.071 | -0.130 | 0.169 | 0.316 | 0.395 |
| Valley and Ridge Sites | 28 | -0.056 | -0.217 | -0.099 | -0.129 | 0.228 |
| All SNP Sites | 14 | **0.168** | -0.036 | **0.969** | 0.512 | 0.195 |
| SNP Siliciclastic Sites | 5 | 0.142 | -0.136 | 0.049 | 0.475 | 0.081 |
| SNP Granitic Sites | 4 | 0.076 | -0.223 | 0.969 | -0.170 | 0.107 |
| SNP Basaltic Sites | 5 | 1.612 | **0.535** | **2.300** | 1.818 | 0.612 |
| **Sulfate (µeq/L)** | | | | | | |
| All Virginia Sites | 65 | 0.028 | **0.333** | 0.021 | **-0.164** | **-0.143** |
| Blue Ridge Sites | 37 | 0.013 | 0.258 | -0.040 | -0.164 | **-0.244** |
| Valley and Ridge Sites | 28 | 0.109 | **0.429** | 0.152 | -0.179 | -0.134 |
| All SNP Sites | 14 | **-0.229** | 0.006 | -0.193 | -0.389 | **-0.395** |
| SNP Siliciclastic Sites | 5 | -0.349 | -0.096 | **-0.214** | -0.775 | -0.361 |
| SNP Granitic Sites | 4 | -0.115 | 0.040 | -0.052 | -0.153 | -0.326 |
| SNP Basaltic Sites | 5 | **-0.246** | 0.107 | -0.151 | -0.381 | **-0.452** |
| **Sum of Base Cations (µeq/L/yr)** | | | | | | |
| All Virginia Sites | 65 | 0.044 | 0.085 | -0.184 | 0.082 | 0.057 |
| Blue Ridge Sites | 37 | 0.007 | -0.002 | -0.221 | 0.221 | 0.037 |
| Valley and Ridge Sites | 28 | 0.064 | 0.294 | -0.130 | 0.016 | 0.151 |
| All SNP Sites | 14 | -0.073 | -0.115 | -0.023 | 0.120 | -0.525 |
| SNP Siliciclastic Sites | 5 | -0.212 | -0.026 | -0.420 | -0.443 | **-0.274** |
| SNP Granitic Sites | 4 | -0.128 | -0.065 | -0.025 | 0.294 | **-0.550** |
| SNP Basaltic Sites | 5 | 0.675 | -0.656 | 0.585 | 1.798 | -0.105 |

Table VI-6. Continued.

| Sites | N sites | Annual Trends | Seasonal Trends | | | |
|---|---|---|---|---|---|---|
| | | | Winter | Spring | Summer | Fall |
| **Nitrate (μeq/L/yr)** | | | | | | |
| All Virginia Sites | 65 | 0.035 | 0.044 | **-0.021** | **0.086** | **-0.012** |
| Blue Ridge Sites | 37 | 0.005 | 0.025 | **-0.043** | -0.007 | **-0.014** |
| Valley and Ridge Sites | 28 | 0.091 | 0.150 | -0.003 | 0.230 | -0.010 |
| All SNP Sites | 14 | -0.298 | -0.127 | **-0.430** | -0.124 | **-0.382** |
| SNP Siliciclastic Sites | 5 | 0.017 | 0.028 | -0.127 | 0.086 | -0.029 |
| SNP Granitic Sites | 4 | -0.205 | -0.237 | **-0.242** | **-0.150** | **-0.031** |
| SNP Basaltic Sites | 5 | **-0.867** | **-1.089** | **-1.165** | -0.151 | **-0.947** |
| **Chloride (μeq/L/yr)** | | | | | | |
| All Virginia Sites | 65 | -0.014 | 0.022 | -0.011 | 0.025 | -0.015 |
| Blue Ridge Sites | 37 | -0.014 | 0.008 | 0.005 | 0.031 | -0.028 |
| Valley and Ridge Sites | 28 | -0.018 | 0.037 | -0.033 | 0.020 | 0.010 |
| All SNP Sites | 14 | **-0.147** | -0.121 | -0.163 | -0.092 | -0.129 |
| SNP Siliciclastic Sites | 5 | **-0.147** | -0.119 | **-0.170** | **-0.123** | -0.129 |
| SNP Granitic Sites | 4 | **-0.172** | -0.172 | -0.129 | -0.092 | -0.190 |
| SNP Basaltic Sites | 5 | -0.095 | -0.078 | -0.052 | 0.032 | -0.093 |
| **Sum of Acid Anions (μeq/L/yr)** | | | | | | |
| All Virginia Sites | 65 | 0.094 | **0.490** | -0.021 | 0.086 | **-0.251** |
| Blue Ridge Sites | 37 | -0.084 | 0.367 | **-0.255** | -0.227 | **-0.355** |
| Valley and Ridge Sites | 28 | 0.197 | **0.717** | 0.197 | 0.305 | -0.080 |
| All SNP Sites | 14 | **-0.619** | -0.411 | **-0.814** | -0.559 | **-0.655** |
| SNP Siliciclastic Sites | 5 | -0.613 | -0.148 | **-0.717** | **-0.343** | **-0.624** |
| SNP Granitic Sites | 4 | **-0.302** | -0.046 | -0.324 | -0.721 | -0.556 |
| SNP Basaltic Sites | 5 | **-1.228** | **-1.445** | **-1.726** | -0.554 | **-1.572** |
| **Hydrogen Ion (μeq/L/yr)** | | | | | | |
| All Virginia Sites | 65 | **0.007** | **0.016** | 0.010 | 0.006 | **-0.004** |
| Blue Ridge Sites | 37 | 0.007 | **0.010** | **0.008** | 0.005 | -0.003 |
| Valley and Ridge Sites | 28 | **0.008** | **0.032** | 0.011 | **0.006** | -0.012 |
| All SNP Sites | 14 | **0.007** | **0.015** | **0.004** | 0.000 | 0.000 |

| Table VI-6. Continued. | | | | | | |
|---|---|---|---|---|---|---|
| Sites | N sites | Annual Trends | Seasonal Trends | | | |
| | | | Winter | Spring | Summer | Fall |
| SNP Siliciclastic Sites | 5 | 0.015 | 0.043 | 0.006 | **-0.038** | -0.054 |
| SNP Granitic Sites | 4 | **0.010** | **0.020** | **0.005** | 0.010 | -0.004 |
| SNP Basaltic Sites | 5 | **0.006** | **0.008** | **0.003** | 0.004 | 0.003 |
| **Calcium Ion (µeq/L/yr)** | | | | | | |
| All Virginia Sites | 65 | 0.078 | 0.151 | 0.031 | 0.076 | 0.048 |
| Blue Ridge Sites | 37 | 0.125 | 0.128 | 0.047 | 0.163 | 0.062 |
| Valley and Ridge Sites | 28 | 0.066 | 0.218 | 0.024 | 0.033 | 0.008 |
| All SNP Sites | 14 | **0.163** | 0.215 | 0.220 | 0.156 | 0.005 |
| SNP Siliciclastic Sites | 5 | **0.161** | **0.314** | 0.053 | 0.088 | **0.062** |
| SNP Granitic Sites | 4 | -0.008 | 0.161 | 0.098 | 0.025 | **-0.261** |
| SNP Basaltic Sites | 5 | 0.422 | -0.084 | **0.413** | 0.972 | 0.009 |
| **Magnesium Ion (µeq/L/yr)** | | | | | | |
| All Virginia Sites | 65 | 0.007 | 0.030 | **-0.041** | 0-082 | 0.024 |
| Blue Ridge Sites | 37 | -0.015 | 0.008 | **-0.048** | 0.004 | -0.004 |
| Valley and Ridge Sites | 28 | 0.041 | 0.114 | -0.033 | 0.112 | 0.127 |
| All SNP Sites | 14 | -0.082 | -0.033 | -0.107 | -0.075 | **-0.179** |
| SNP Siliciclastic Sites | 5 | **-0.273** | -0.057 | **-0.283** | -0.270 | **-0.256** |
| SNP Granitic Sites | 4 | -0.103 | -0.004 | 0.017 | -0.020 | **-0.116** |
| SNP Basaltic Sites | 5 | 0.204 | -0.356 | 0.057 | 0.625 | -0.026 |
| **Sodium Ion (µeq/L/yr)** | | | | | | |
| All Virginia Sites | 65 | -0.020 | -0.043 | **-0.076** | -0.005 | 0.025 |
| Blue Ridge Sites | 37 | -0.018 | -0.103 | **-0.086** | 0.168 | 0.034 |
| Valley and Ridge Sites | 28 | **-0.030** | -0.026 | **-0.073** | -0.012 | 0.016 |
| All SNP Sites | 14 | -0.121 | **-0.226** | -0.188 | 0.039 | -0.123 |
| SNP Siliciclastic Sites | 5 | **-0.163** | **-0.226** | **-0.234** | **-0.063** | **-0.112** |
| SNP Granitic Sites | 4 | **-0.127** | **-0.352** | **-0.209** | 0.274 | -0.219 |
| SNP Basaltic Sites | 5 | 0.086 | -0.214 | 0.002 | 0.208 | -0.058 |

Table VI-6. Continued.

| Sites | N sites | Annual Trends | Seasonal Trends | | | |
|---|---|---|---|---|---|---|
| | | | Winter | Spring | Summer | Fall |
| **Potassium Ion (µeq/L/yr)** | | | | | | |
| All Virginia Sites | 65 | **-0.043** | -0.013 | **-0.040** | **-0.070** | **-0.095** |
| Blue Ridge Sites | 37 | -0.034 | -0.019 | -0.018 | -0.025 | **-0.085** |
| Valley and Ridge Sites | 28 | **-0.067** | -0.007 | **-0.067** | **-0.087** | **-0.103** |
| All SNP Sites | 14 | 0.007 | 0.048 | 0.019 | 0.020 | **-0.075** |
| SNP Siliciclastic Sites | 5 | -0.006 | 0.074 | 0.031 | -0.105 | **-0.207** |
| SNP Granitic Sites | 4 | **0.033** | 0.048 | 0.059 | **0.089** | **-0.047** |
| SNP Basaltic Sites | 5 | -0.025 | 0.043 | 0.006 | 0.009 | **-0.085** |
| **Silica (µm/L/yr)** | | | | | | |
| All Virginia Sites | 65 | **-0.079** | -0.107 | **-0.120** | **-0.151** | 0.115 |
| Blue Ridge Sites | 37 | **-0.130** | -0.171 | **-0.285** | **-0.151** | 0.104 |
| Valley and Ridge Sites | 28 | **-0.057** | **-0.083** | -0.017 | -0.169 | 0.157 |
| All SNP Sites | 14 | **-0.601** | **-0.472** | **-0.340** | **-0.863** | **-0.639** |
| SNP Siliciclastic Sites | 5 | **-0.242** | -0.098 | -0.307 | -0.097 | -0.218 |
| SNP Granitic Sites | 4 | **-0.705** | **-0.647** | **-0.340** | -1.096 | **-0.639** |
| SNP Basaltic Sites | 5 | **-0.972** | **-0.607** | -0.404 | **-1.384** | -1.623 |
| **CALK[a] (µeq/L/yr)** | | | | | | |
| All Virginia Sites | 65 | 0.042 | -0.302 | -0.104 | 0.138 | 0.294 |
| Blue Ridge Sites | 37 | 0.177 | -0.290 | 0.116 | 0.602 | 0.295 |
| Valley and Ridge Sites | 28 | -0.171 | -0.347 | -0.317 | -0.380 | 0.258 |
| All SNP Sites | 14 | **0.294** | **0.164** | **0.439** | 0.668 | 0.076 |
| SNP Siliciclastic Sites | 5 | 0.177 | 0.131 | **0.309** | 0.206 | 0.007 |
| SNP Granitic Sites | 4 | 0.211 | -0.128 | 0.270 | 0.623 | 0.006 |
| SNP Basaltic Sites | 5 | **1.805** | **0.911** | **2.311** | 2.352 | 1.141 |

[a] CALK is calculated ANC (CALK=SBC-SAA)

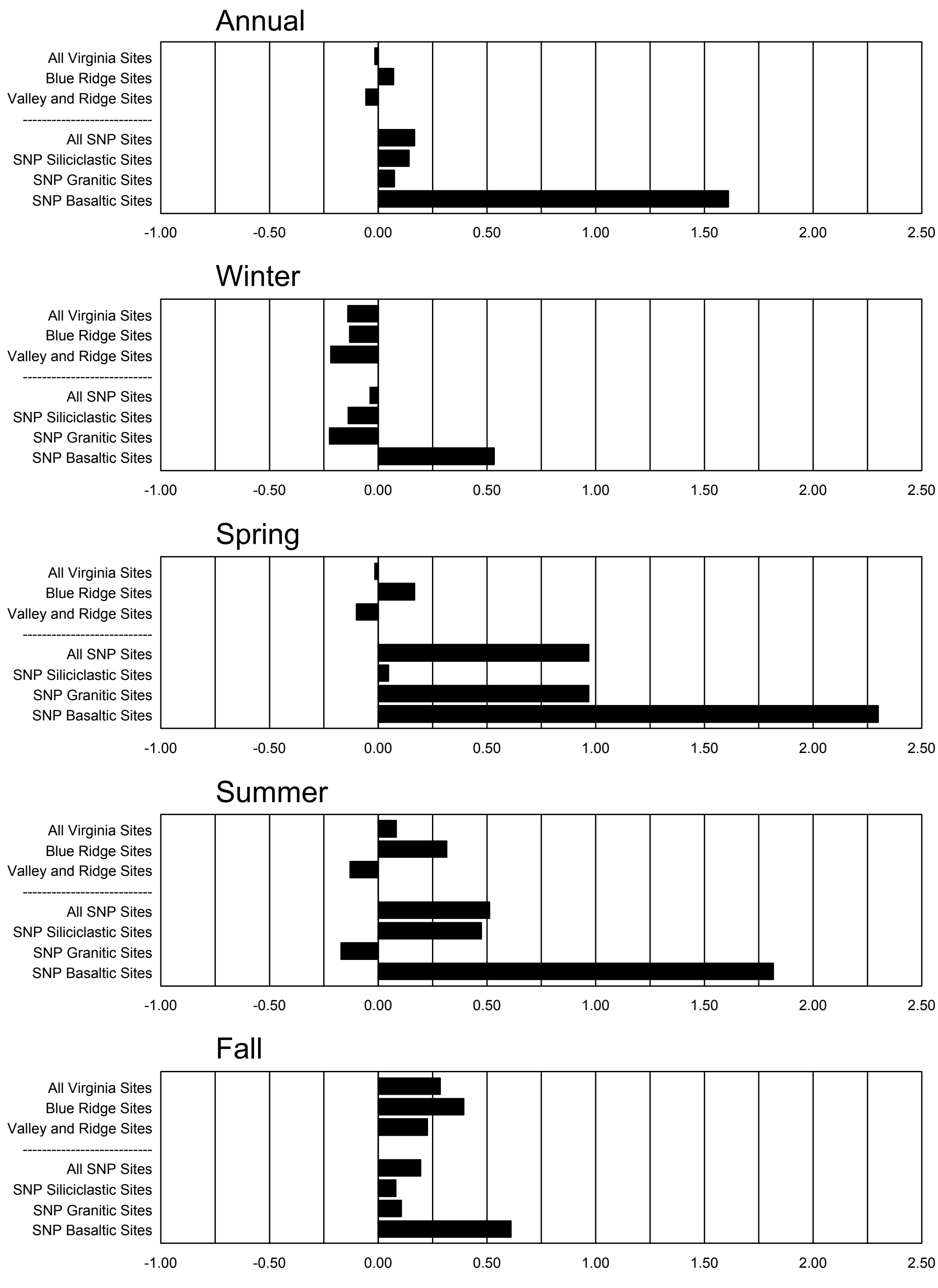



Figure VI-8. Median values of annual and seasonal trends (in μeq/L) in streamwater ANC concentrations among VTSSS and SWAS watersheds: 1988-2001. The median values are from distributions of ANC trends determined for streams within classes defined by physiography or lithology. The annual trends are based on simple linear regressions on all quarterly data for 14 years (n=56). Seasonal trends are based on individual quarterly values for 14 years (n=14).

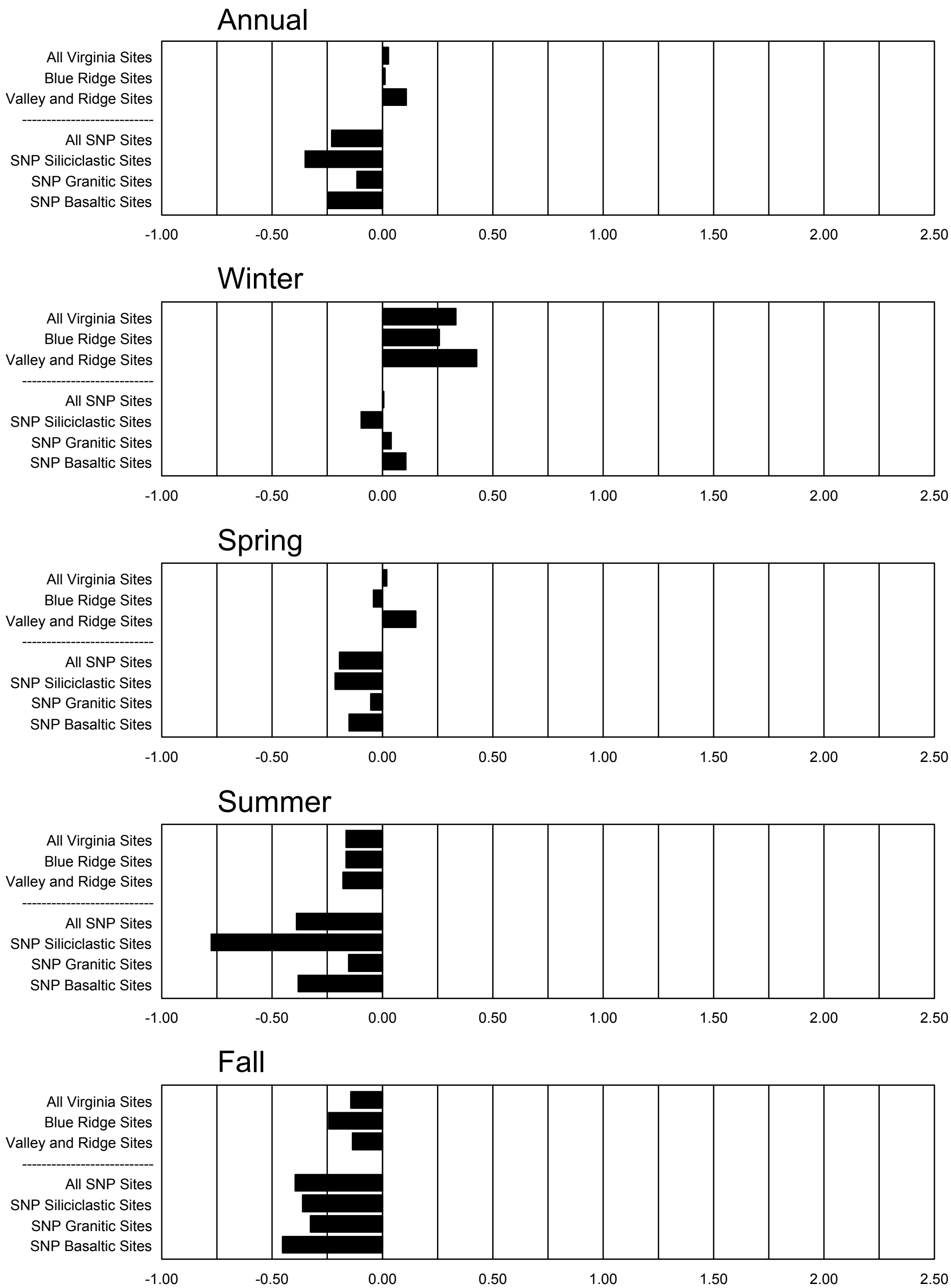



Figure VI-9. Median values of annual and seasonal trends in streamwater $SO_4^{2-}$ concentrations (in μeq/L) among VTSSS and SWAS watersheds: 1988-2001. The median values are from distributions of ANC trends determined for streams within classes defined by physiography or lithology. The annual trends are based on simple linear regressions on all quarterly data for 14 years (n=56). Seasonal trends are based on individual quarterly values for 14 years (n=14).

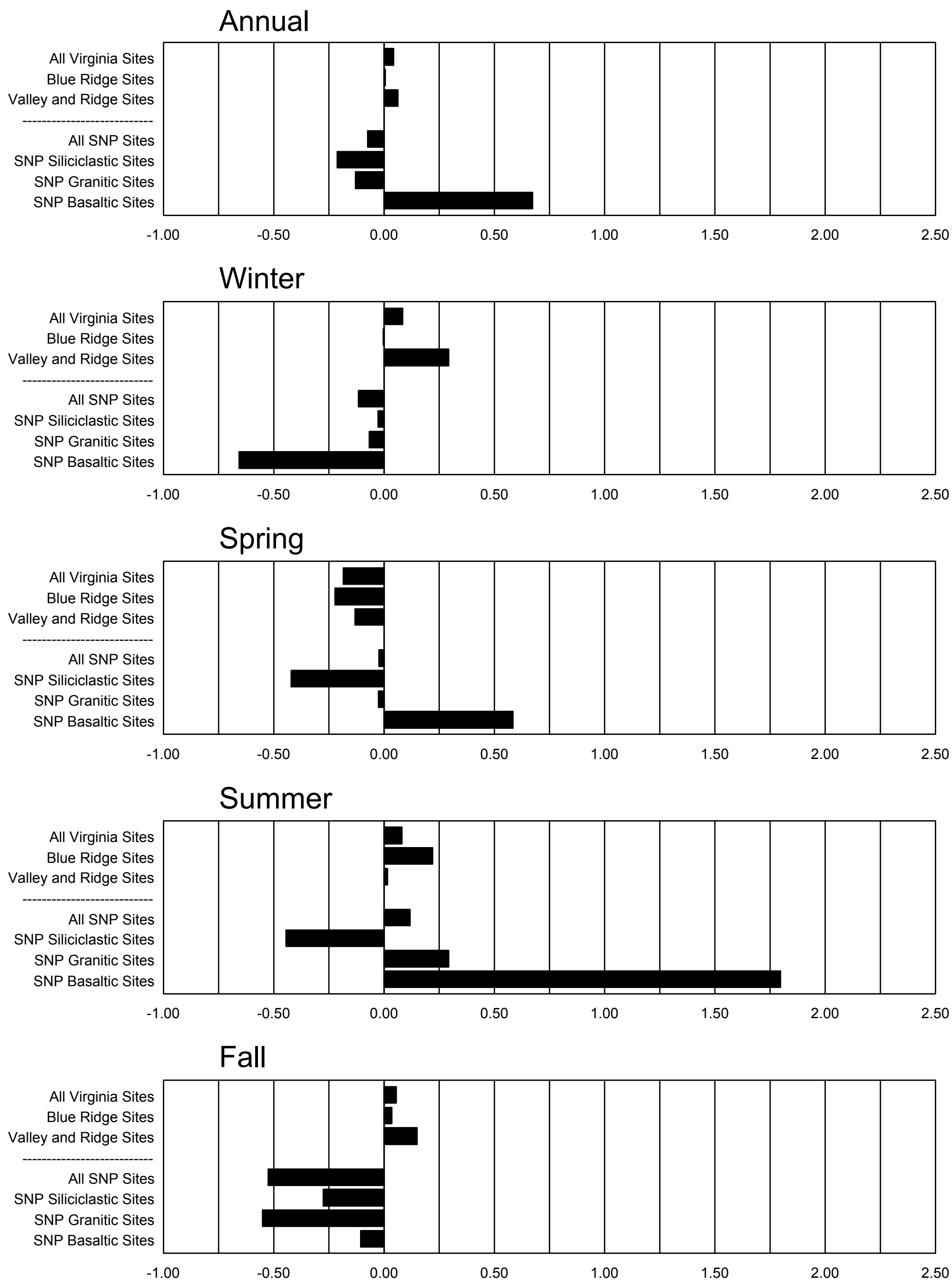



Figure VI-10. Median values of annual and seasonal trends in streamwater SBC concentrations (in µeq/L) among VTSSS and SWAS watersheds: 1988-2001. The median values are from distributions of ANC trends determined for streams within classes defined by physiography or lithology. The annual trends are based on simple linear regressions on all quarterly data for 14 years (n=56). Seasonal trends are based on individual quarterly values for 14 years (n=14).

6. Although most of the observed median trend values for these key parameters are small and generally not significant, geographic, lithologic, and seasonal patterns are evident.

ANC Trends

The median annual trend in ANC was positive for the group of 14 study streams in SHEN, as well as for all of the lithologically defined subsets of streams (Figure VI-8). In contrast, the median ANC decreased on an annual basis for the 65 study streams in western Virginia. Thus, although there is some evidence for some recovery from acidification effects on streamwater composition among the SHEN streams, there is evidence for continuing acidification among streams in the larger region, which encompasses those in SHEN. This observation of continuing acidification among the study streams in the larger western Virginia region is consistent with trend results reported by Stoddard et al. (2003), who evaluated trends among the same set of streams for the 1990-2000 period. It should be noted that the observed median annual trends in ANC in both SHEN and the western Virginia region are quite small; when considered over the 14-year period, the median ANC change in streamwaters is only +2.4 μeq/L in SHEN and –0.2 μeq/L in western Virginia.

It should also be noted that the observed median annual trends differ for western Virginia streams classified by physiographic province. Median trends were negative for streams in the Valley and Ridge province and positive for streams in the Blue Ridge province, which includes the SHEN area. Thus, there is some evidence for a recovery gradient between the two provinces, as well as between the park and western Virginia as a whole.

Additional patterns in ANC trends were evident among the different seasons. Most notably, the median trend values in winter contrasted with those of the other seasons, generally showing a negative trend in median ANC. Only the SHEN streams associated with basaltic bedrock showed a positive value for median ANC trend in winter. In contrast, the median trend values for the fall season were positive for all of the defined classes of streams. These observed seasonal differences in median ANC trends may have biological significance because winter is the period of the year when the most acid-sensitive life stages of the brook trout (eggs and fry) are present in the streams of SHEN and western Virginia (Figure VI-11).

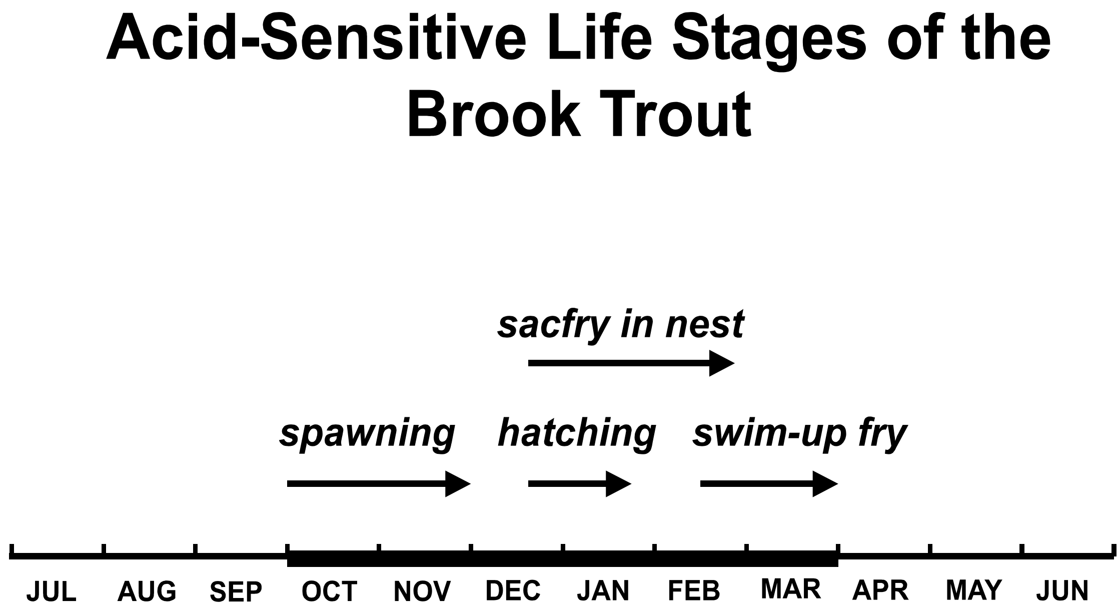



Figure VI-11. Life stages of brook trout.

<u>Sulfate Trends</u>

The level of $SO_4^{2-}$ leaching, which is the principal acidifying process, and the availability of exchangeable base cations, which serve to neutralize acidity, determine both acidification and recovery of streams in the central Appalachian region. Plots of median trends in streamwater $SO_4^{2-}$ (Figure VI-9) are consistent with the observation that changes in $SO_4^{2-}$ mobility are largely driving both the acidification and recovery processes in the streams of SHEN and the adjacent mountainous region. The median annual trend in $SO_4^{2-}$ concentration was negative for all the streams in SHEN, including each of the lithologically-defined subgroups. A negative median annual trend in $SO_4^{2-}$ concentration was associated with a positive median annual trend in ANC.

Again, a different pattern is evident for the median annual trends in $SO_4^{2-}$ among the streams in the larger western Virginia region. The observed median annual trend in $SO_4^{2-}$ concentration was positive for the regional streams. For the Virginia streams, as well as the streams in the Valley and Ridge province, a positive median annual trend in $SO_4^{2-}$ concentration was associated with a negative median annual trend in ANC. It thus appears that recent differences in streamwater ANC trends between SHEN and the larger western Virginia region, although relatively small in terms of absolute magnitude, may be largely attributed to differences in streamwater $SO_4^{2-}$ trends between the two defined areas.

A plot of $SO_4^{2-}$ trends for individual study streams in the western Virginia region (Figure VI-12) suggests that these observed differences in $SO_4^{2-}$ trends can be explained as a consequence of S retention dynamics. As indicated in Figure VI-12, the streams with the largest negative trends in $SO_4^{2-}$ concentration over the 14-year period, including many in the park, were generally those with higher median $SO_4^{2-}$ concentrations. This observation is consistent with the expectation that streamwater $SO_4^{2-}$ concentrations in the southern Appalachian Mountains in general are determined by the S adsorption properties of watershed soils and the level of watershed exposure to S deposition. For watersheds with high S deposition and relatively little retention, streamwater $SO_4^{2-}$ concentrations will be high. Decreases in S deposition may then result in decreases in streamwater $SO_4^{2-}$ concentrations. For watersheds that more strongly retain S, streamwater $SO_4^{2-}$ concentrations will be lower. Decreases in S deposition may then either result in no change in streamwater $SO_4^{2-}$ concentrations or $SO_4^{2-}$ concentrations may actually continue to increase as the retention capacity of watershed soils is depleted.

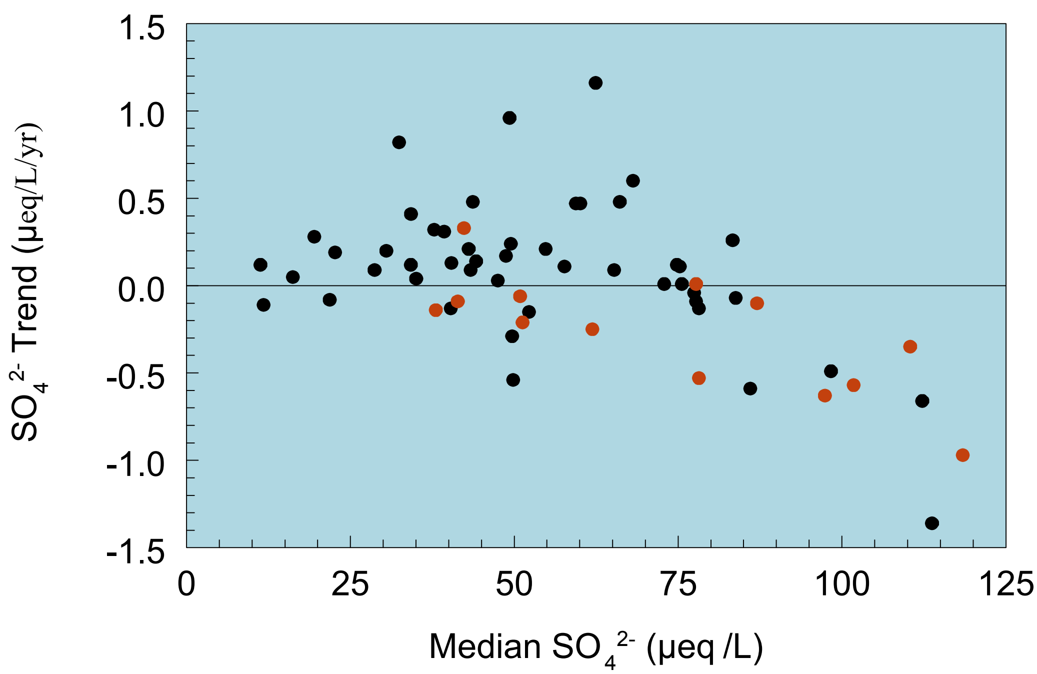



Figure VI-12. Trends in streamwater $SO_4^{2-}$ concentrations in relation to median $SO_4^{2-}$ concentrations for VTSSS and SWAS streams. Trends and medians are based on quarterly sampling data (1988-2001). SWAS study streams (located in SHEN) are indicated with red symbols.

Seasonal patterns in median $SO_4^{2-}$ concentration trends indicate that the difference in ANC change between winter and the rest of the year is also largely a function of $SO_4^{2-}$ trends. The largest and most general increases in median $SO_4^{2-}$ concentrations were observed during winter. Sulfate concentration trends were generally negative in other seasons.

SBC Trends

The plots of median trends in the sum of base cation concentrations are also informative (Figure VI-10), and suggest that base cation availability is a limiting factor with respect to recovery of streams in SHEN and western Virginia. The median annual trends in the sum of base cations were decreasing in all SHEN streams except streams associated with basaltic bedrock. As indicated in Table VI-1 and Figure VI-4, streams on basaltic bedrock had relatively high base cation concentrations and soils on basaltic bedrock had relatively high base cation availability. For the streams on relatively base-poor siliciclastic or granitic bedrock, the observed decrease in the sum of base cations coincident with the decrease in $SO_4^{2-}$ concentrations suggested that low availability of base cations limited recovery of ANC.

It is also notable that although there was much seasonal variation in median trends in the sum of base cations, the SHEN streams with the most consistently negative trends were on siliciclastic bedrock. This may be an indication of base cation depletion in watershed soils, given that the soils on siliciclastic bedrock had notably low base cation availability (see Figure VI-4). For this subset of streams in particular, ANC recovery may be limited by base cation availability and additional acidification may be expected to occur as the watershed base cation supplies are further depleted, especially if S deposition remains relatively high.

*c. Summary of Trends in Streamwater Chemistry in SHEN*

In summary, it appears that the streams in SHEN are showing signs of recovery, whereas the streams in the larger western Virginia region are not. Moreover, the patterns of trends in ANC and $SO_4^{2-}$ are consistent with expectations for recovery. Considered in relation to the regional-scale analysis of Stoddard et al. (2003), these observations suggest that evidence for decreasing $SO_4^{2-}$ concentrations and increasing ANC in SHEN streams may reflect a north-to-south recovery gradient in the eastern United States. It should be noted, however, that the changes in both ANC and $SO_4^{2-}$ concentrations in SHEN and western Virginia are small compared to those reported for other regions by Stoddard et al. (2003), are confounded by seasonal differences, and in many cases are not statistically significant.

## 3. Biological Effects

Extensive information is available on the effects of acidification on aquatic communities in general. In addition, some studies have been conducted within SHEN and throughout western Virginia. Whole system experiments, mesocosm experiments, and field surveys have demonstrated major shifts in species composition and decreases in species richness with increasing acidity. The range of sensitivity to acidification varies among fish species, and to a greater extent among invertebrate species. Some sensitive species are lost at even moderate pH levels, around pH 6.0. In lakes, some important zooplankton predators are affected at pH 5.6-5.9. Some sensitive mayflies and fish (e.g. fathead minnow [*Baetis lapponicus*]) are lost at pH 5.6- 6.0 (Baker and Christensen 1991). Toxic mechanisms are well established for fish, and for invertebrates to a lesser degree (Baker et al. 1991).

### *a. Acidification Effects on Aquatic Invertebrates in SHEN*

Benthic macroinvertebrates have been monitored in SHEN streams since 1986 as part of the Long-Term Ecological Monitoring System (LTEMS). Moeykens and Voshell (2002) recently examined these data, comparing them with streamwater chemistry in the park. Their analysis was based on interpretation of 10 chemical and physical variables measured at 89 sites in SHEN (28 low-ANC sites and 61 higher-ANC sites) for which macroinvertebrate data were available. They compared their results for SHEN streams with similar analyses for 45 sites (13 low-ANC sites and 32 higher-ANC sites) elsewhere in the Blue Ridge ecoregion of Virginia. The macroinvertebrate communities in both data sets were characterized with 12 robust variables thought to represent the ecological function and composition of these communities. Moeykens and Voshell (2002) concluded that the higher-ANC streams in SHEN had “superior ecological condition” which was comparable to the best that can be found among the streams in the broader Blue Ridge ecoregion. However, they also concluded that acidification of streamwater causes the only conspicuous degradation of macroinvertebrate communities in some low-ANC SHEN streams. Other disturbances, such as fire and flood, did not appear to have had noticeable long-term effects on the streams. Moeykens and Voshell (2002) concluded that acidified streams in

SHEN host fewer invertebrate taxa and fewer functional groups than streams with higher pH and ANC. Similar findings were reported earlier for SHEN streams by Feldman and Connor (1992).

Though not part of SHEN, the proximity of the St. Mary's River (30 km south of SHEN) makes the recent analyses of changes in macroinvertebrate communities in that stream pertinent to this analysis for SHEN streams. As described by Kauffman et al. (1999), the record for St. Mary's River provides a unique opportunity to compare reliable macroinvertebrate data on an acidified stream over a 60-year time span. Surber (1951) collected the earliest benthic data for St. Mary's River. Starting in August of 1935, and continuing for two years, he collected 20 samples per month from the river's main stem. Subsequent data were collected by the Virginia Department of Game and Inland Fisheries (VDGIF) in 1976 and then biennially beginning in 1986 (Kauffman et al. 1999) using methods comparable to those used for the 1930s collections. The VDGIF data were collected at six evenly spaced locations extending the length of the main stem above the Wilderness boundary. The later collections were made in June, and only June data are used in the following comparisons.

As summarized by Kauffman et al. (1999), changes in the St. Mary's River benthic community are consistent with streamwater acidification. Whereas 29-32 benthic taxa were documented in the 1930s, no more than 22 benthic taxa were observed in the 1990s. Acid-sensitive taxa have generally declined in abundance and some may have been extirpated. In contrast, certain acid-tolerant taxa have increased in abundance, apparently due to less competition from acid-sensitive taxa.

The total abundance of mayfly (Ephemeroptera) larva in the St. Mary's River has dramatically decreased over the 60-year period, and two of the mayfly genera, Paraleptophlebia and Epeorus, were last collected in 1976. Mayflies are known to decline in species abundance and richness with increasing acidity (Peterson and Van Eeckhautz 1992, Kobuszewski and Perry 1993). The total abundance of caddisfly (Trichoptera) larva also declined dramatically over the 60-year period of record. Baker et al. (1990b) indicated that caddisflies exhibit a wide range of response to acidity, with some species affected by even moderate acidity levels. The total abundance of the larva of the stonefly (Plecoptera) genera Leuctra/Alloperla has dramatically increased over the 60-year period. Increased abundance of these stoneflies in acidified waters has been well documented (Kimmel and Murphy 1985). Another insect family that has prospered in St. Mary's River is the midge (Chironomidae), whose larval population has increased ten fold since the 1930s collections. Increased midge abundance in acidified waters has also been well documented (Kimmel and Murphy 1985, Baker et al. 1990b).

Many stream invertebrate communities are dominated by early life stages of insects that have great dispersal abilities as flying adults. Thus, with many local sources of colonists and the possibility of continual re-colonization, invertebrate biodiversity in affected streams in SHEN is probably continually suppressed by acidity levels. In all likelihood (by analogy to the St. Mary's study), currently acidified SHEN streams hosted more diverse invertebrate communities in pre-industrial times. Given the relatively rapid recovery time (about 3 years) of stream invertebrate communities from disturbance, more productive and diverse invertebrate communities might be among the first positive results of lower acid deposition. On the other hand, if streamwater ANC declines further, we can expect macroinvertebrate diversity to decrease.

Species – ANC Relationships for Aquatic Invertebrates in SHEN Streams

In light of this previous work, the quantitative relationships between invertebrate communities and streamwater quality in SHEN streams were analyzed. The data from the SHEN-LTEMS aquatic macroinvertebrate data base (summarized in Section II.D.2) and the quarterly streamwater data (described in Section VI.B.1) were used in this analysis. The objective was to describe and quantify the correlations between streamwater chemistry (primarily ANC) and various measures of invertebrate community status in the streams.

The 14 SWAS streams in the park (Figure VI-1) have quarterly water quality data extending back to 1988. The means, maxima, and minima of solute concentrations in these streams were calculated for the period 1988 to 2001 for use in the analyses (Table VI-7). Interquartile values for these streamwater chemistry samples are given in Table (VI-1). Note that the quarterly samples actually cover the 14 water years from Oct. 1987 to Sept. 2001.

The LTEMS benthic invertebrate data for the period June 1988 through June 2000 were selected for comparison with water quality data. There are five phyla of benthic macroinvertebrates represented in the samples from SHEN streams (Annelida, Arthropoda, Mollusca, Nematoda, and Platyhelminthes). Because of their importance to park streams and known sensitivity of many taxa to acidification, this analysis was limited to the data collected on aquatic insects (class Insecta of the phylum Arthropoda).

Table VI-7. Minimum, average and maximum ANC values in the 14 SHEN study streams during the period 1988 to 2001 for all quarterly samples. The data cover 14 water years except for VT75 (11 years).

| Site ID | Watershed | ANC (ueq/L) | | |
|---|---|---|---|---|
| | | Minima | Mean | Maxima |
| Siliciclastic Bedrock Class | | | | |
| DR01 | Deep Run | -9.5 | 2.9 | 24.4 |
| VT35 (PAIN) | Paine Run | -1.3 | 7.0 | 19.5 |
| VT36 | Meadow Run | -11.4 | -1.3 | 6.2 |
| VT53 | Twomile Creek | 2.8 | 15.2 | 38.6 |
| WOR1 | White Oak Run | 3.6 | 27.7 | 58.6 |
| | | | | |
| Granitic Bedrock Class | | | | |
| NFDR | North Fork Dry Run | 22.5 | 65.6 | 187.8 |
| VT58 | Brokenback Run | 44.0 | 87.9 | 155.4 |
| VT59 (STAN) | Staunton River | 46.1 | 87.3 | 189.4 |
| VT62 | Hazel River | 54.4 | 95.6 | 163.6 |
| | | | | |
| Basaltic Bedrock Class | | | | |
| VT51 | Jeremys Run | 93.7 | 217.2 | 542.5 |
| VT60 (PINE) | Piney River | 118.7 | 228.4 | 382.9 |
| VT61 | North Fork Thornton River | 156.2 | 286.6 | 452.9 |
| VT66 | Rose River | 94.4 | 150.2 | 229.2 |
| VT75 | White Oak Canyon Run | 81.2 | 138.6 | 237.2 |

There are nine orders of aquatic insects present in the SHEN LTEMS samples: Coleoptera, Collembola, Diptera, Ephemeroptera, Hemiptera, Megaloptera, Odonata, Plecoptera, and Trichoptera. From these nine orders of aquatic insects, 79 families have been collected in SHEN streams. Not all families are present in each stream. The total number of insect families found in a given stream during the sampling period varied from 21 to 56 (Table II-2). Of the nine orders of aquatic insects found in SHEN streams, there were three which were most abundant both in terms of frequency of occurrence in samples and total numbers of individuals collected: Ephemeroptera (mayflies); Plecoptera (stoneflies); and Trichoptera (caddisflies). The use of these three orders as indicators of acidification response in streams is well established. A combined metric based on all three families, the Ephemeroptera-Plecoptera-Trichoptera (EPT) index, is one measure of stream macroinvertebrate community integrity. This is the total number of families in the three insect orders present in a collection. These orders contain families of varying acid sensitivity so the index value (the number of families) is lower at acidified sites (c.f., Section III.C.2, SAMAB, 1996).

Strong relationships for all three orders were observed between mean and minimum streamwater ANC and the number of families in each order (Figure VI-13). The total numbers of individuals in each order was also related strongly to the mean and minimum ANC values of the 14 streams (Figure VI-14). The EPT index provides a single measure of all three orders and was, as expected, also strongly related to mean and minimum streamwater ANC (Figure VI-15).

*b. Acidification Effects on Fish in SHEN*

Although there are known differences in acid sensitivity among fish species, experimentally-determined acid sensitivities are available for only a minority of freshwater fish species. For example, of 30 species of fish found in SHEN, the critical pH is known for only nine (Table VI-8). Baker and Christensen (1991) reported critical pH values for 25 species of fish. They defined critical pH as the threshold for significant adverse effects on fish populations. The reported range of pH values represents the authors' estimate of the uncertainty of this threshold. The range of response within species depends on differences in sensitivity among life stages, and on different exposure concentrations of calcium ($Ca^{2+}$) and Al. These ranges, based on multiple studies for each species, are shown in Table VI-8. To cite a few examples, blacknose dace (*Rhinichthys atratulus*) is regarded as very sensitive to acid stress, because population loss due to acidification has been documented in this species at pH values as high as 6.1; in field bioassays, embryo mortality has been attributed to acid stress at pH values as high as 5.9. Embryo mortality has occurred in common shiner (*Luxilus cornutus*) at pH values as high as 6.0. Although the critical pH range for rainbow trout (*Oncorhynchus mykiss*) is designated as 4.9-5.6, adult and juvenile mortality have occurred at pH values as high as 5.9. Brown trout (*Salmo trutta*) population loss has occurred over the pH range of 4.8-6.0, and brook trout fry mortality has occurred over the range of 4.8-5.9 (Baker and Christensen 1991). Relative sensitivities can be suggested by regional surveys as well, although interpretation of such data is complicated by factors that correlate with elevation. Such factors, including habitat complexity and refugia from high-flow conditions, often vary with elevation in parallel with acid sensitivity. It is noteworthy, however that about half of the 53 fish species found in Adirondack Mountain waters in New York never occur at pH values below 6.0 (Kretzer et al. 1989, Driscoll et al. 2001a); for those species whose acid tolerances are unknown, it is likely that acid sensitivity is responsible for at least some of these absences. It is the difference in acid tolerance among

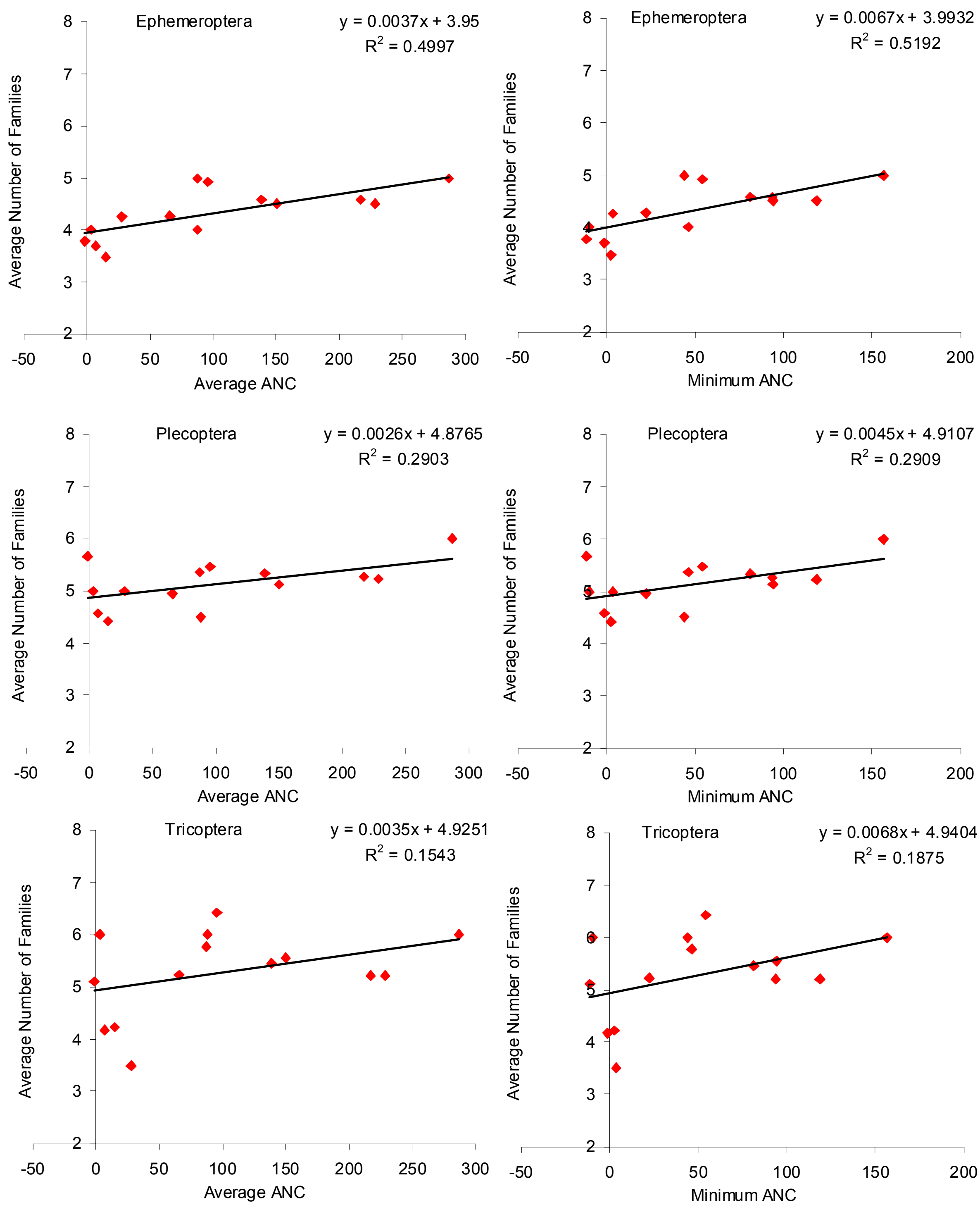



Figure VI-13. Average number of families of aquatic insects in a sample for each of 14 streams in SHEN versus the mean (left) or minimum (right) ANC of each stream. The stream ANC values are based on quarterly samples from 1988 to 2001. The invertebrate samples are contemporaneous. Results are presented for the orders Ephemeroptera (top), Plecoptera (center), and Tricoptera (bottom). The regression relationship and correlation are given on each diagram.

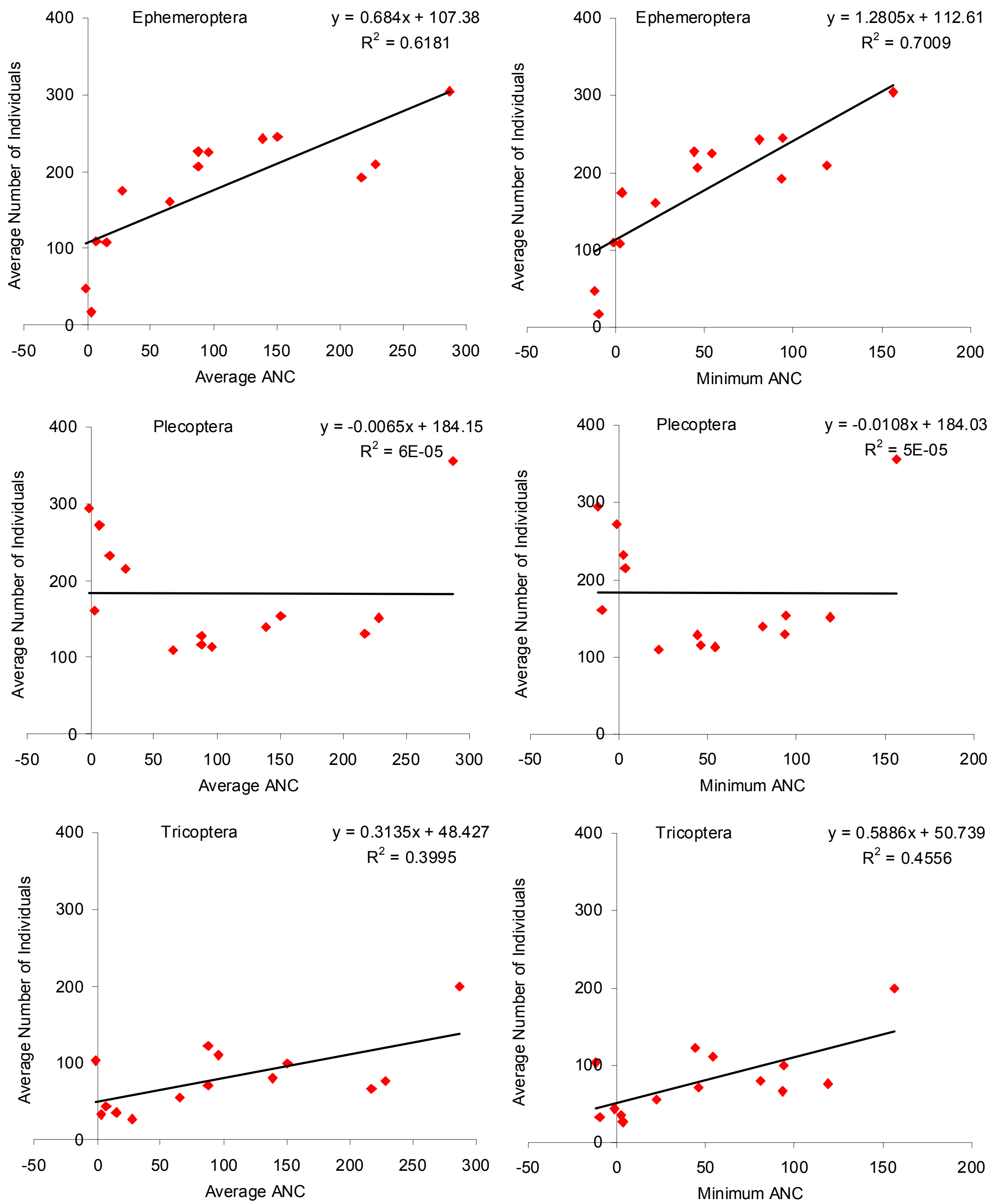
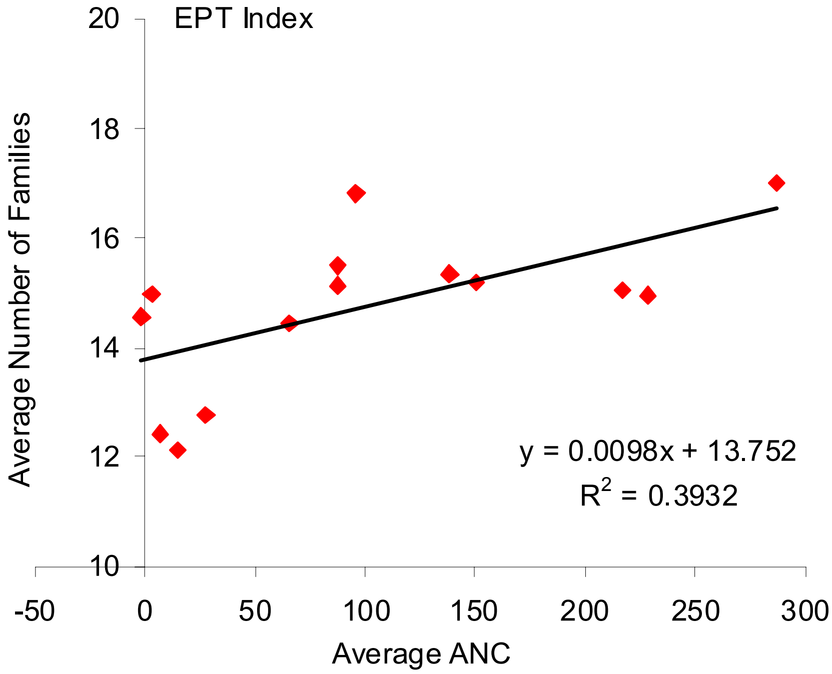



Figure VI-14. Average total number of individuals of aquatic insects in a sample for each of 14 streams in SHEN versus the mean (left) or minimum (right) ANC of each stream. The stream ANC values are based on quarterly samples from 1988 to 2001. The invertebrate samples are contemporaneous. Results are presented for the orders Ephemeroptera (top), Plecoptera (center), and Tricoptera (bottom). The regression relationship and correlation are given on each diagram.



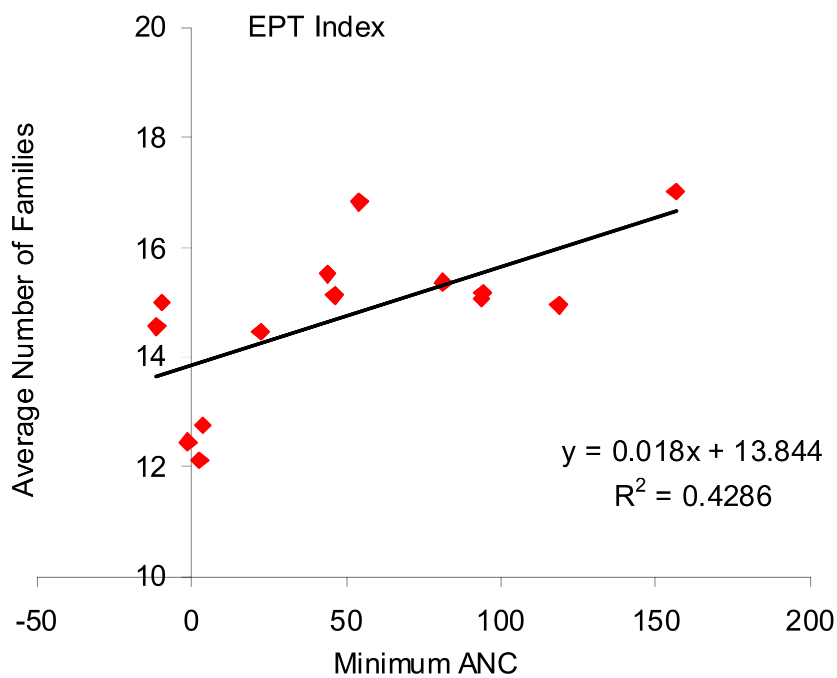




Figure VI-15. Average EPT index in a sample for each of 14 streams in SHEN versus the mean (top) or minimum (bottom) ANC of each stream. The stream ANC values are based on quarterly samples from 1988 to 2001. The invertebrate samples are contemporaneous. The regression relationship and correlation are given on each diagram.

Table VI-8. Critical pH thresholds for fish species of SHEN. (Source: Bulger et al. 1999)

| Common Name | Latin Name | Family | Critical pH[a] Threshold |
|---|---|---|---|
| American Eel | *Anguilla rostrata* | Anguillidae | |
| Mtn. Redbelly Dace | *Phoxinus oreas* | Cyprinidae | |
| Rosyside Dace | *Clinostomus funduloides* | Cyprinidae | |
| Longnose Dace | *Rhinichthys cataractae* | Cyprinidae | |
| Blacknose Dace | *Rhinichthys atratulus* | Cyprinidae | 5.6 to 6.2 |
| Central Stoneroller | *Campostoma anomalum* | Cyprinidae | |
| Fallfish | *Semotilus corporalis* | Cyprinidae | |
| Creek Chub | *Semotilus atromaculatus* | Cyprinidae | 5.0 to 5.4 |
| Cutlips Minnow | *Exoglossum maxillingua* | Cyprinidae | |
| River Chub | *Nocomis micropogon* | Cyprinidae | |
| Bluehead Chub | *Nocomis leptocephalus* | Cyprinidae | |
| Common Shiner | *Luxilus cornutus* | Cyprinidae | 5.4 to 6.0 |
| Potomac Sculpin | *Cottus girardi* | Cottidae | |
| Northern Hogsucker | *Hypentelium nigricans* | Catostomidae | |
| Torrent Sucker | *Thoburnia rhothocea* | Catostomidae | |
| White Sucker | *Catastomus commersoni* | Catostomidae | 4.7 to 5.2 |
| Margined Madtom | *Noturus insignis* | Ictaluridae | |
| Brook Trout | *Salvelinus fontinalis* | Salmonidae | 4.7 to 5.2 |
| Brown Trout | *Salmo trutta* | Salmonidae | 4.8 to 5.4 |
| Tiger Trout[b] | *Salmo X Salvelinus* | Salmonidae | |
| Rainbow Trout | *Oncorhynchus mykiss* | Salmonidae | 4.9 to 5.6 |
| Mottled Sculpin | *Cottus bairdi* | Cottidae | |
| Bluntnose Minnow | *Pimephales notatus* | Cyprinidae | |
| Rock Bass | *Ambloplites rupestris* | Centrarchidae | 4.7 to 5.2 |
| Smallmouth Bass | *Micropterus dolomieui* | Centrarchidae | 5.0 to 5.5 |
| Largemouth Bass | *Micropterus salmoides* | Centrarchidae | |
| Redbreast Sunfish | *Lepomis auritus* | Centrarchidae | |
| Pumpkinseed | *Lepomis gibbosus* | Centrarchidae | |
| Johnny Darter | *Etheostoma nigrum* | Percidae | |
| Tesselated Darter | *Etheostoma olmstedi* | Percidae | |
| Fantail Darter | *Etheostoma flabellare* | Percidae | |
| Greenside Darter[b] | *Etheostoma blennioides* | Percidae | |

[a] threshold for serious adverse effects on populations (from Baker & Christensen 1991)
[b] rare (6-10 individuals)

species that produces a gradual decline in species richness as acidification progresses, with the most sensitive species lost first. Some Blue Ridge streams can become too acidic even for brook trout, as evidenced by the absence of the species from streams with mean pH < 5.0 in Great Smoky Mountains National Park (Elwood et al. 1991).

A direct outcome of fish population loss as a result of acidification is a decline in species richness (the total number of species in a lake or stream). This appears to be a highly predictable outcome of regional acidification, although the pattern and rate of species loss varies from region to region. Baker et al. (1990a) discussed 10 selected studies which documented this phenomenon, with sample sizes ranging from 12 to nearly 3,000 lakes and streams analyzed per study. An excellent example occurs in the Adirondacks. Fully 346 of 1469 lakes surveyed supported no fish at all. These lakes were significantly lower in pH, dissolved $Ca^{2+}$, and ANC than lakes hosting one or more species of fish. Among lakes with fish, there was an unambiguous relationship between the number of fish species and lake pH, ranging from about one species per lake for lakes having pH less than 4.5 to about six species per lake for lakes having pH > 6.5 (Kretzer et al. 1989, Driscoll et al. 2001b).

Relatively less is known about changes in fish biomass, density and condition (robustness of individual fish) which occur in the course of acidification. Such changes result in part from both indirect and direct interactions within the fish community. Loss of sensitive individuals within species (such as early life stages) may reduce competition for food among the survivors, resulting in better growth rates, survival, or condition. Similarly, competitive release (increase in growth or abundance subsequent to removal of a competitor) may result from the loss of a sensitive species, with positive effects on the density, growth, or survival of competitor population(s) of other species (Baker et al. 1990b). In some cases where acidification continued, transient positive effects on size of surviving fish were shortly followed by extirpation (Bulger et al. 1993).

ANC criteria have been used for evaluation of potential acidification effects on fish communities. The utility of these criteria lies in the association between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress, in particular pH, $Ca^{2+}$, and Al. Bulger et al. (2000) developed ANC thresholds for brook trout response to acidification in forested headwater catchments in western Virginia (Table VI-9). Note that because brook trout are comparatively acid tolerant, adverse effects on many other fish species should be expected at relatively higher ANC values.

Table VI-9. Streamwater acid neutralizing capacity (ANC) categories for brook trout response (Bulger et al. 2000).

| Response Category | ANC Class | ANC Range µeq/L | Brook Trout Response |
|---|---|---|---|
| Suitable | Not acidic | >50 | Reproducing brook trout populations expected where habitat suitable |
| Indeterminate | Indeterminate | 20-50 | Extremely sensitive to acidification; brook trout response variable |
| Marginal | Episodically acidic | 0-20 | Sub-lethal and/or lethal effects on brook trout possible |
| Unsuitable | Chronically acidic | <0 | Lethal effects on brook trout probable |
| Note: ANC range based on volume-weighted annual mean. | | | |

The early life stages of brook trout are most sensitive to adverse impacts from acidification (Bulger et al. 2000). These early life stages occur in SHEN throughout the cold season in general, and the winter in particular (Figure VI-11). For this reason, data presented in Section VI.B.2 suggesting ongoing winter season acidification trends for streams within SHEN are of particular concern.

Adult brook trout in SHEN streams are more tolerant of acidity than are adult blacknose dace. For both species, the early life stages are more sensitive than the adults, and brook trout young are actually more sensitive than blacknose dace adults (Bulger et al. 1999). Blacknose dace spawn during summer and the eggs and very young fry are therefore somewhat insulated from the most acidic episodes, which typically occur during cold-season, high-flow conditions.

The recent three-year FISH study of stream acidification in SHEN demonstrated negative effects on fish from both chronic and episodic acidification (Bulger et al. 1999). Biological differences in low- versus high-ANC streams included species richness, population density, condition factor (a measure of robustness in individual fish), age, size, and field bioassay survival. Of particular note is that both episodic and chronic mortality occurred in young brook trout exposed in a low-ANC stream, but not in a high-ANC stream (MacAvoy and Bulger 1995), and that blacknose dace in low-ANC streams were in poor condition relative to blacknose dace in higher-ANC streams (Dennis et al 1995, Dennis and Bulger 1995).

A statistically-robust relationship between acid-base status of streamwater and fish species richness was shown in SHEN as well. As an element of the FISH project (Bulger et al. 1999), numbers of fish species were compared among 13 SHEN streams spanning a range of pH/ANC conditions. There was a highly significant ($p<0.0001$) relationship between stream acid-base status (during the seven-year period of record) and fish species richness among the 13 streams, such that the streams having the lowest ANC hosted the fewest species (Figure VI-16). Although the number of streams in the study was small, the results were consistent with other studies (Baker et al. 1990a); this is the first, however, to provide a statistically-robust analysis among multiple streams in the southeastern United States.

In addition to acid-base status, stream size and drainage area are very important for fish diversity for a number of reasons. In this regard the FISH project streams appeared to be similar. The study streams in the FISH project were all first or second order streams within SHEN. They all may be regarded as high-gradient, well-oxygenated streams having large pebble/cobble substrates. All were shaded by riparian vegetation across their width during the study, although a later flood denuded the banks of one stream. Long riffles typically alternate with deeper pools; there are occasional small cascades. Width and depth vary with discharge, but all are wadeable at their widest point (typically at or near the park boundary) and upstream in summer.

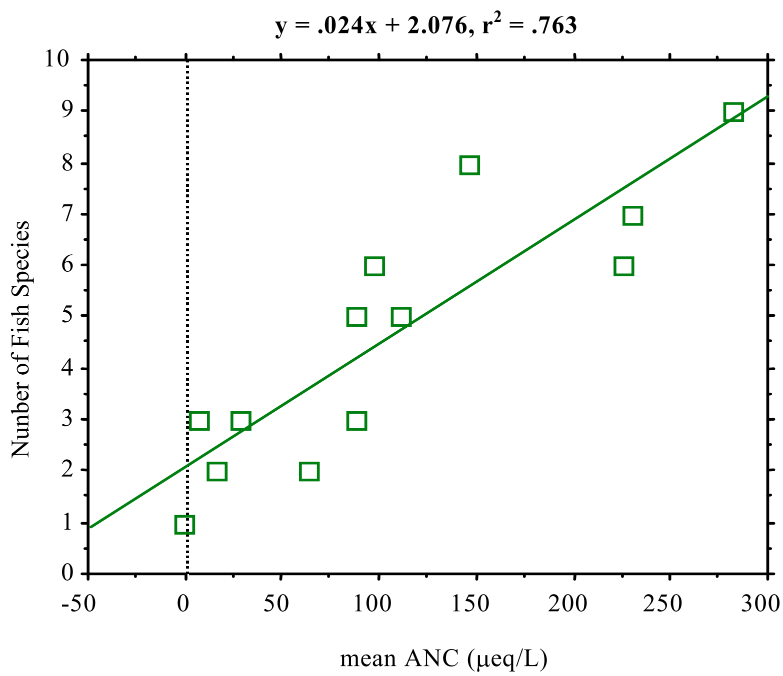



Figure VI-16. Number of fish species among 13 streams in SHEN. Values of ANC are means based on quarterly measurements, 1987-94. The regression analysis showed a highly significant relationship ($p \leq 0.0001$) between mean stream ANC and number of fish species. Streams having ANC consistently < 75 µeq/L had three or fewer species.

Median streamwater ANC values and watershed areas are shown in Table VI-10 for the 13 streams used by Bulger et al. (1999) to develop the relationship between ANC and fish species richness shown in Figure VI-16. Despite the overall similarities, these study streams vary in watershed area by a factor of 10. The streams that have larger watershed areas generally have more fish species than the streams having smaller watershed areas. All of the "rivers" have watersheds larger than 10 $km^2$ and ANC higher than 75 µeq/L. In contrast, the majority (but not all) of the "runs" have watershed area smaller than 10 $km^2$ and ANC less than 20 µeq/L. All of the streams that have watershed areas smaller than 10 $km^2$ have three or fewer known species of fish present. The ANC of the smaller streams is determined largely by the underlying geology. All of the streams having larger watersheds (> 10 $km^2$) have three or more known fish species; seven of nine have five or more species; and the average number of fish species is six. One of the streams in the larger-watershed category that had fewer than five species of fish (Paine Run, three species) had very low ANC. There is no clear distinction between river and run, but it is clear that as small streams in SHEN combine and flow into larger streams and eventually to

Table VI-10. Median streamwater ANC and watershed area of streams in SHEN that have water chemistry and fish species richness data.

| Site ID | Watershed Area ($km^2$) | Median ANC (µeq/L) | Number of Fish Species |
|---|---|---|---|
| **Smaller Watersheds (< 10 $km^2$)** | | | |
| North Fork Dry Run | 2.3 | 48.7 | 2 |
| Deep Run | 3.6 | 0.3 | N.D.[a] |
| White Oak Run | 4.9 | 16.2 | 3 |
| Two Mile Run | 5.4 | 10.0 | 2 |
| Meadow Run | 8.8 | -3.1 | 1 |
| **Larger Watersheds (>10 $km^2$)** | | | |
| Brokenback Run | 10.1 | 74.4 | 3 |
| Staunton River | 10.6 | 76.8 | 5 |
| Piney River | 12.4 | 191.9 | 7 |
| Paine Run | 12.7 | 3.7 | 3 |
| Hazel River | 13.2 | 86.8 | 6 |
| White Oak Canyon | 14.0 | 119.3 | 7 |
| N. Fork Thornton River | 18.9 | 249.1 | 9 |
| Jeremy's Run | 22.0 | 158.5 | 6 |
| Rose River | 23.6 | 133.6 | 8 |

[a] No data were available regarding the number of fish species in Deep Run.

rivers, two things happen: acid-sensitivity *generally* declines, and habitat *generally* becomes suitable for additional fish species.

This does not imply that either acid-base status or fish species richness is controlled solely by either acidic deposition or watershed area. It appears that fish species richness is controlled by multiple factors, of which both acidification and watershed area can be important. Watershed area might be important in this context because smaller watersheds may contain smaller streams having less diversity of habitat, more pronounced impacts on fish from high flow periods, or lower food availability. Such issues interact with other stresses, including acidification, to determine overall habitat suitability.

As another component of the FISH project, condition factor was compared in populations of blacknose dace in SHEN in 11 streams spanning a range of pH/ANC conditions (Bulger et al. 1999). Figure VI-17 shows the highly significant relationship between mean stream pH and condition factor in blacknose dace. Note that the four populations represented on the left side of the figure all have mean pH values within or below the range of critical pH values, at which negative populations effects are likely for the species (Baker and Christensen 1991). That poor condition is related to population survival is suggested by the extirpation in 1997 of the blacknose dace population from the stream (Meadow Run) with the lowest pH and ANC (J. Atkinson, pers. comm.; Figure VI-17).

The results of the condition factor comparisons among the 11 streams indicated that the mean length-adjusted condition factor of fish from the stream with the lowest ANC was about 20% lower than that of the fish in best condition. No previous studies have reported changes in condition factor of blacknose dace during acidification. Comparisons with the work of Schofield and Driscoll (1987) and Kretser et al. (1989) suggest that pH in the low-pH SHEN streams is near or below the limit of occurrence for blacknose dace populations in the Adirondack region of New York.

As with reduced growth rates observed for acid-stressed populations of invertebrates, smaller blacknose dace body size could result from direct toxicity (e.g., elevated energy use to compensate for sublethal ionoregulatory stress) or from reduced access to food or lower food quality (Baker et al. 1990a). Primary productivity is low in headwater streams and lower still in softwater headwaters, which are more likely to be acidified. Production of invertebrates is likely to be low in such streams as well, even though terrestrial inputs of food are much more

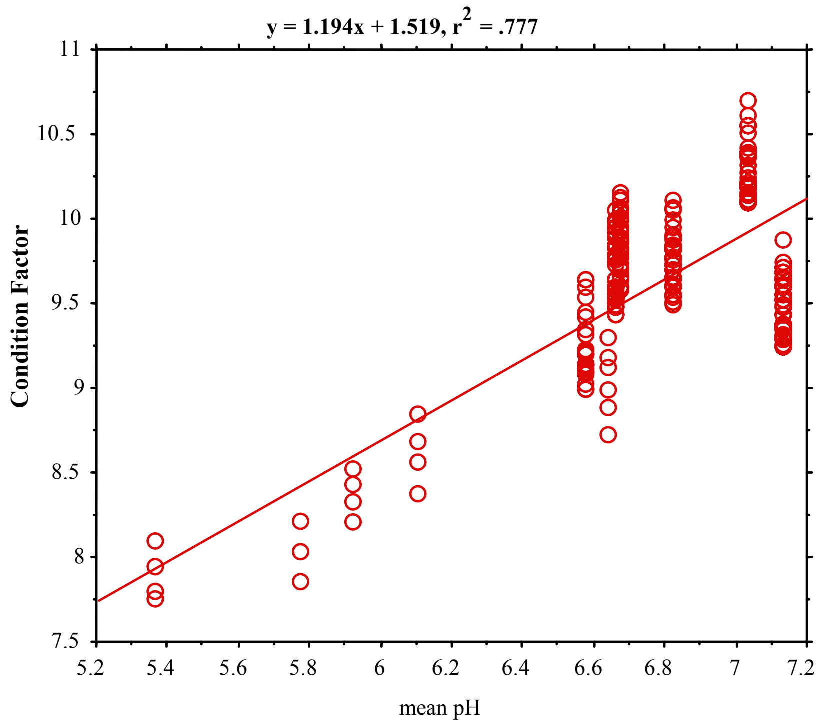



Figure VI-17. Length-adjusted condition factor (K), a measure of body size in blacknose dace (*Rhinichthys atratulus*) among 11 populations (n=442) in SHEN. Values of pH are means based on quarterly measurements, 1991-94; K was measured in 1994. The regression analysis showed a highly significant relationship ($p \leq 0.0001$) between mean stream pH and body size, such that fish from acidified streams were smaller than fish from circumneutral streams.

important for insect productivity in forested catchments than in-stream production (Wallace et al. 1992). Thus, lower food availability cannot be ruled out as a potential contributor to lowered condition in SHEN blacknose dace populations. Nevertheless, reduced growth rates have been attributed to acid stress in a number of other fish species, including Atlantic salmon, chinook salmon, lake trout, rainbow trout, brook trout, brown trout, and Arctic char. Furthermore, the blacknose dace population in poorest condition in SHEN occurred in a stream with mean pH below the minimum recorded for blacknose dace populations in Vermont, New Hampshire, Maine and New York (Baker et al. 1990a). The four blacknose dace populations in poorest condition in SHEN occurred in streams at or below the critical pH for the species, where adverse effects due to acidification are likely to be detectable at the population level (Baker et al 1990a). Consequently, acid stress is probably at least partly responsible for the lower condition of blacknose dace populations in SHEN, though lower food availability, either resulting from the nature of softwater streams or exacerbated by acidification, cannot be ruled out.

It is possible that smaller body size in blacknose dace (and the lake trout cited above) is the result of energy transfer from somatic growth to physiological maintenance, secondary to chronic sublethal acidification stress. It is well known that chronic sublethal stress reduces growth in fish, as well as reproductive success (Wedemeyer et al. 1990). Chronic sublethal stress caused by pH levels up to 6.0 may have serious effects on wild trout populations. There is an energy cost in maintaining physiological homeostasis; the calories used to respond to stress are a part of the fish's total energy budget and are unavailable for other functions, such as growth (Schreck 1981, 1982).

The energy costs to fish for active iono-osmoregulation can be substantial (Farmer and Beamish 1969, Bulger 1986). The concentrations of serum electrolytes (such as sodium [$Na^+$] and chloride [$Cl^-$]) are many times higher (often 100-fold higher) in fish blood than in the freshwaters in which they live. The active uptake of these ions occurs at the gills. Because of the steep gradient in $Na^+$ and $Cl^-$ concentrations between the blood and freshwater, there is constant diffusional loss of these ions, which must be replaced by energy-requiring active transport. Low pH increases the rate of passive loss of blood electrolytes (especially $Na^+$ and $Cl^-$); and Al elevates losses of $Na^+$ and $Cl^-$ above the levels due to acid stress alone (Wood 1989). Since dace in an acidified stream maintain whole-body $Na^+$ at levels similar to dace in a high-ANC stream (Dennis and Bulger 1995), despite probable higher gill losses of electrolytes due to acid/Al stress, then the homeostatic mechanisms at the gill responsible for maintaining blood electrolyte levels must work harder and use more energy to maintain these levels.

An additional component of the FISH project used multiple bioassays over three years in one of the low-ANC streams to determine the effect of stream baseflow and acid episode stream chemistry on the survival of brook trout eggs and fry (MacAvoy and Bulger 1995). Simultaneous bioassays took place in mid- and higher-ANC reference streams. Acid episodes (with associated low pH and elevated Al concentrations, and high streamwater discharge) induced rapid mortality in the low-ANC stream, while the test fish in the higher-ANC stream, experiencing only the high streamwater discharge, survived (Bulger et al. 1999).

The effects of acidification on fish have been well documented for the St. Mary’s River (Bugas et al. 1999). Fourteen fish species have been collected in St. Mary’s River since 1976;

only four remained as of 1998. Rosyside dace (*Clinostomus funduloides*) and torrent sucker (*Thoburnia rhothocea*) were last present in 1996; Johnny darter (*Etheostoma nigrum*) and brown trout were last present in 1994; rainbow trout and longnose dace (*Rhinichthys cataractae*) were last present in 1992; bluehead chub (*Nocomis leptocephalus*) and smallmouth bass (*Micropterus dolomieui*) were last present in 1990 and 1988, respectively; white sucker (*Catastomus commersoni*) and central stoneroller (*Campostoma anomalum*) were last present in 1986. Of the four remaining species, three (blacknose dace, fantail darter [Etheostoma flabellare]), and mottled sculpin [*Cottus bairdi*]) have declined in density and/or biomass; the fourth remaining species is brook trout, the region's most acid tolerant species; this population has fluctuated, and reproductive success has been sporadic. Blacknose dace, once abundant throughout the river, remain only at the lowest sampling station, which has the highest pH, and at such low numbers (five individuals in 1998) that they might be strays from downstream. For some of the species (smallmouth bass, white sucker, the three trout, and blacknose dace) the critical pH is known (see Table VI-8), and their decline and/or extirpation, given the pH of the river, is not surprising. Based on trend analysis over the period 1987-1997, the St. Mary's River, near SHEN, is continuing to acidify (Webb and Deviney 1999).

Recent analyses (Bulger et al. 1998, 2000) divided Virginia's streams into four categories of acid-base status, to compare the number of streams in each category at present with estimated numbers in pre-industrial times and in the future. Within SHEN, streams that are chronically or episodically acidic are the most likely to have experienced adverse biological effects from acidic deposition to date. They are also the streams most at risk for future damage. These streams are found primarily on siliciclastic bedrock. See listing of known acidic and low-ANC streams within the park in Appendix D.

**4. Episodic Acidification Effects**

Values of annual average or spring season average water chemistry are typically used to represent conditions at a given site for purposes of characterization. However, streamwater chemistry undergoes substantial temporal variability, especially in association with hydrological episodes. During such episodes, which are driven by rainstorms and/or snowmelt events, both discharge (streamflow volume per unit time) and water chemistry change, sometimes dramatically. This is important because streams may in some cases exhibit chronic chemistry that is suitable for aquatic biota, but experience occasional episodic acidification with lethal consequences (c.f., Wigington et al. 1993).

Data regarding episodic variability in streamwater ANC for six intensively-studied sites within SHEN for the period 1993 to 1999 are presented in Figure VI-18. The minimum measured ANC each year at each site (which generally is recorded during a large hydrological episode) is plotted against the median spring ANC for that year at that site. Sites that exhibited median spring ANC below about 20 µeq/L (Paine Run, White Oak Run, Deep Run) generally had minimum measured ANC about 10 µeq/L lower than median spring ANC. In contrast, at the high-ANC Piney River site (median spring ANC > 150 µeq/L), the minimum measured ANC was generally more than about 40 µeq/L lower than the respective median spring ANC. At sites

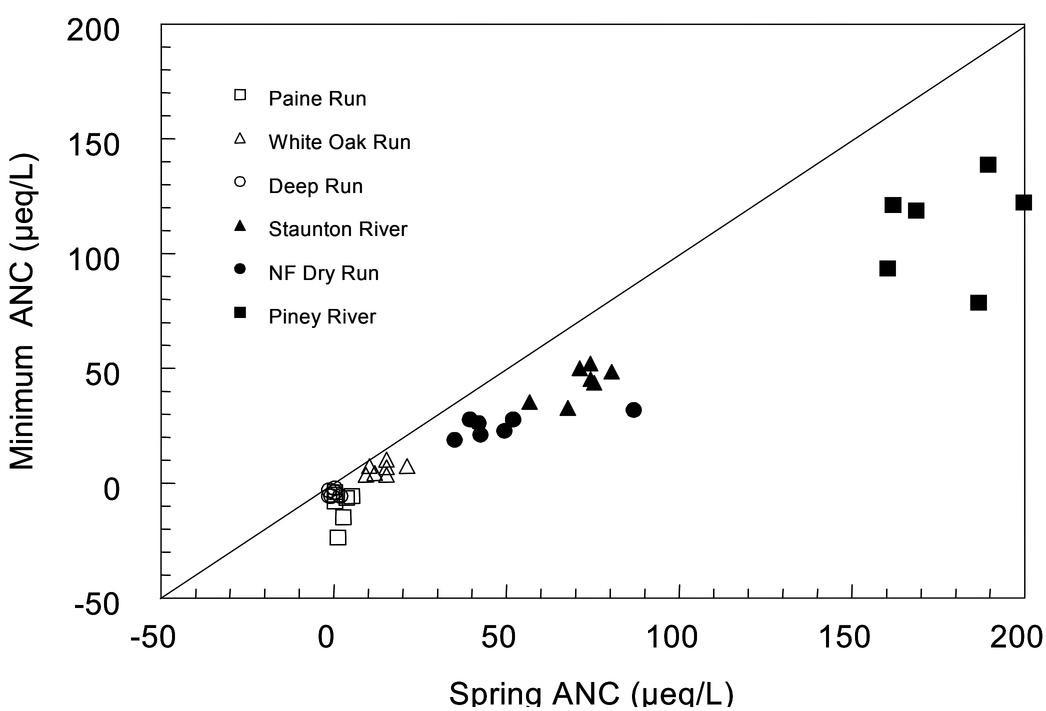



Figure VI-18. Minimum streamwater ANC sampled at each site during each year versus median spring ANC for all samples collected at that site during that spring season. Data are provided for all intensively-studied streams within SHEN during the period 1993-1999. A 1:1 line is provided for reference. The vertical distance from each sample point upwards to the 1:1 line indicates the ANC difference between the median spring value and the lowest sample value for each site and year.

having intermediate ANC values, with median spring ANC in the range of about 30 to 90 μeq/L, the minimum ANC measured each year was generally about 20 to 30 μeq/L lower than the respective median spring ANC. Thus, there is a rather clear pattern of larger episodic ANC depressions in streams having higher median ANC and smaller episodic ANC depressions in streams having lower median ANC. The two sites that had median spring ANC between about 0 and 10 μeq/L consistently showed minimum measured values below 0. Streams having low chronic ANC can be expected to experience relatively small episodic ANC depressions. However, those depressions often result in minimum ANC values that are associated with toxicity to aquatic biota.

The routing of water as it flows through a watershed determines the degree of contact with acidifying or neutralizing materials and therefore influences (along with soils and bedrock characteristics) the amount of episodic acidification that occurs. In any given watershed, surface water ANC may vary in time depending upon the proportion of the flow that has contact with deep versus shallow soil horizons; the more subsurface contact, the higher the surface water ANC (Turner et al. 1990). This can be attributed in part to higher base saturation and greater $SO_4^{2-}$ adsorption capacity in subsurface soils. It may also be related to the accumulation in the upper soil horizons of acidic material derived from atmospheric deposition and decay processes (Lynch and Corbett 1989, Turner et al. 1990). Storm flow and snowmelt are often associated with episodes of extreme surface water acidity due to an increase in the proportion of flow derived from water that has moved laterally through the surface soil without infiltration to deeper soil horizons (Wigington et al. 1990). Episodic acidification may be the limiting condition for aquatic organisms in central Appalachian streams that are marginally suitable for aquatic life under baseflow conditions.

A number of studies of episodic acidification have been conducted in streams within SHEN. Miller-Marshall (1993) analyzed data from the SWAS for the period 1988-1991 for White Oak Run, North Fork Dry Run, Deep Run, and Madison Run, and also conducted a field experiment in 1992 at White Oak Run and North Fork Dry Run. Acid anion flushing was the predominant acidification mechanism during hydrological episodes. Base cation dilution frequently also played a large role, depending on the underlying bedrock geology and baseflow ANC. The ratio of ΔSBC/ΔANC varied from 0.5 at Madison Run (median spring baseflow ANC = 63 μeq/L) to -1.4 at Deep Run (median spring baseflow ANC = 1 μeq/L). Ratios were intermediate (0.2 and

0.3, respectively) at North Fork Dry Run (median spring baseflow ANC = 40 μeq/L) and White Oak Run (median spring baseflow ANC = 16 μeq/L). Thus, at the site exhibiting the lowest baseflow ANC (Deep Run), base cations increased during episodes. At the other sites, base cation concentrations were diluted during episodes, with the greatest dilution occurring in the streams that were highest in baseflow ANC (Miller-Marshall 1993).

There are several different mechanisms of episodic acidification in operation in the streams in SHEN, depending at least in part on the bedrock geology of the stream. Eshleman and Hyer (2000) estimated the contribution of each major ion to observed episodic ANC depressions in Paine Run, Staunton River, and Piney River during a three-year period. During the study, 33 discrete storm events were sampled and water chemistry values were compared between antecedent baseflow and the point of minimum measured ANC (near peak discharge). The relative contribution of each ion to the ANC depressions was estimated using the method of Molot et al. (1989), which normalized the change in ion concentration by the overall change in ANC during the episode. At the low-ANC (≈ 0) Paine Run site on siliciclastic bedrock, increases in $NO_3^-$ and $SO_4^{2-}$, and to a lesser extent organic acid anions, were the primary causes of episodic acidification. Base cations tended to compensate for most of the increases in acid anion concentration. ANC declined by 3 to 21 μeq/L (median 7 μeq/L) during the episodes studied. At the intermediate-ANC (≈ 60 to 120 μeq/L) Staunton River site on granitic bedrock, increases in $SO_4^{2-}$ and organic acid anions, and to a lesser extent $NO_3^-$, were the primary causes of episodic acidification. Base cation increases compensated these changes to a large degree, and ANC declined by 2 to 68 μeq/L during the episodes (median decrease in ANC was 21 μeq/L). At the high-ANC (≈150 to 200 μeq/L) Piney River site on basaltic (69%) and granitic (31%) bedrock, base cation concentrations declined during episodes ( in contrast with the other two sites where base cation concentrations increased). Sulfate and $NO_3^-$ usually increased. The change in ANC during the episodes studied ranged from 9 to 163 μeq/L (median 57 μeq/L; Eshleman and Hyer 2000). Changes in base cation concentrations during episodes contributed to the ANC of Paine Run, had little impact in Staunton River, and consumed ANC in Piney River (Hyer 1997).

The relative importance of the major processes that contribute to episodic acidification varies among the streams within SHEN, in part as a function of bedrock geology and baseflow streamwater ANC. Sulfur-driven acidification was an important contributor to episodic loss of

ANC at all three sites, probably because S adsorption by soils occurs to a lesser extent during high-flow periods. This is due, at least in part, to diminished contact between drainage water and potentially adsorbing soils surfaces. Dilution of base cation concentrations was most important at the high-ANC site.

Similar conclusions were reached by Miller-Marshall (1993). Acid anion flushing was the predominant acidification mechanism during episodic acidification. Base cation dilution also played a large role for most of the watersheds, but the extent of its importance depended largely on the underlying bedrock.

The importance of $NO_3^-$ to episodic acidification is a relatively recent development, attributed to the effects of gypsy moth infestation in many watersheds within the park (Webb et al. 1995, Eshleman et al. 1999). Consumption of foliage by the moth larvae converted foliar N, which is normally tied up in long-term N cycling processes, into more labile N forms on the forest floor.

Eshleman et al. (1999) concluded that episodic acidification of streams in SHEN is controlled by a complex set of natural, anthropogenic, and disturbance factors that together produce a transient response that varies dramatically from watershed to watershed. They further hypothesized that the results of recent studies in the park can be largely explained by a biogeochemical response to forest disturbance by gypsy moth larvae, which temporarily overwhelmed the normal controls on N and base cation dynamics.

The most acidic conditions in SHEN streams occur during high-flow periods, in conjunction with storm or snowmelt runoff. The general relationship between flow level and ANC is evident in Figure VI-19, which plots ANC measurements against flow for three intensively-studied streams representing the major bedrock types in the park. The response of all three streams is similar in that most of the lower ANC values occur in the upper range of flows levels. However, consistent with observations by Eshleman (1988), the minimum ANC values that occur in response to high flow are related to baseflow ANC values. Paine Run (siliciclastic bedrock) had a mean weekly ANC value of about 6 μeq/L and often had high-flow ANC values that were less than 0 μeq/L. Staunton River (granitic bedrock) had a mean weekly ANC value of about 82 μeq/L and had only a few high-flow ANC values less than 50 μeq/L. Piney River (basaltic bedrock) had a mean weekly ANC value of 217 μeq/L and no values as low as 50 μeq/L.

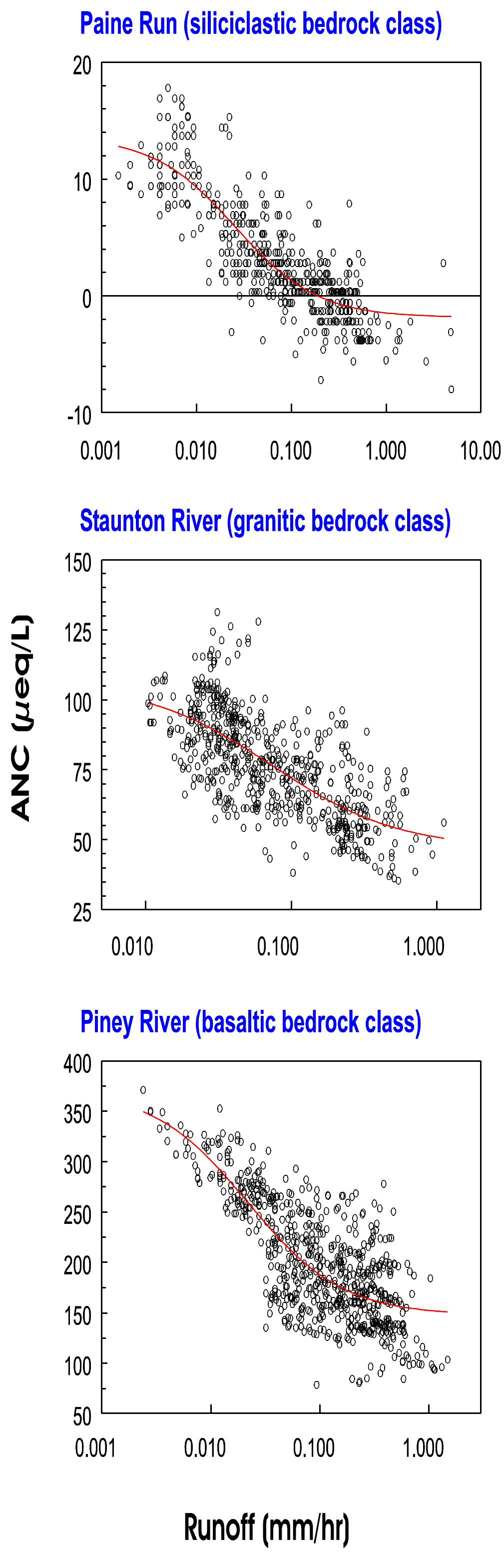



Figure VI-19. Relationship between ANC and runoff for streamwater samples collected at intensively-studied sites in SHEN. The data represent samples collected during the 1992-1997 period.

Previous studies have shown that mobilization of dissolved Al during episodic acidification is a primary cause of fish mortality in streams that have low ANC under baseflow conditions (Wigington et al. 1993). Streams with higher ANC during baseflow are less likely to become sufficiently acidic during episodes to bring much Al into solution. Figure VI-20 provides an example of changes in ANC, pH, and dissolved Al that occurred in Paine Run, Staunton River, and Piney River during a high-flow episode in January 1995. Under baseflow conditions, ANC at the Paine Run site was above 0 μeq/L, pH was above 5.5, and Al concentration was less than 25 μg/L. Discharge levels increased dramatically during the episode, resulting in depression of ANC to less than 0 μeq/L, pH values less than 5.5, and an increase in Al concentration to near 75 μg/L, above the threshold for adverse effects on some species of aquatic biota. That same episode also resulted in substantial declines in ANC in the granitic (Staunton River) and basaltic (Piney River) watersheds. However, ANC values at these two sites were relatively high prior to the episode (about 75 and 175 μeq/L, respectively) and did not decline to below about 50 μeq/L during the episode at either site, and pH values remained above 6.0 and 6.5, respectively (Figure VI-20).

It is notable, however, that Al concentrations at the Staunton River site increased from less than 10 μg/L to about 25 μg/L during the episode. This is somewhat surprising given that Al has very low solubility at pH values above 6.0. Similarly elevated Al concentrations at relatively high pH values have been observed during other high-runoff events in Staunton River (e.g., Bulger et al.1999). This may simply indicate that the sampling frequency has been insufficient to capture the pH extremes that occur during the high-runoff episodes. Another explanation is that Al may be mobilized in more acidic parts of the watershed and then remain in solution at the sampling location despite the higher pH. If so, the range of Al concentrations in streamwater within the watershed probably include higher values than are observed at the sampling site. This latter explanation is supported by the observation that lower streamwater ANC and pH values generally occur at upstream locations within the primary study watersheds (see Tables VI-1 and VI-3). For Staunton River, in particular, the observed within-watershed variation in streamwater ANC during the 1992 survey (see Figure VI-2) was substantial; although ANC was 67 μeq/L at the downstream sampling site, ANC was below 50 μeq/L at 41% of the upstream sampling sites.

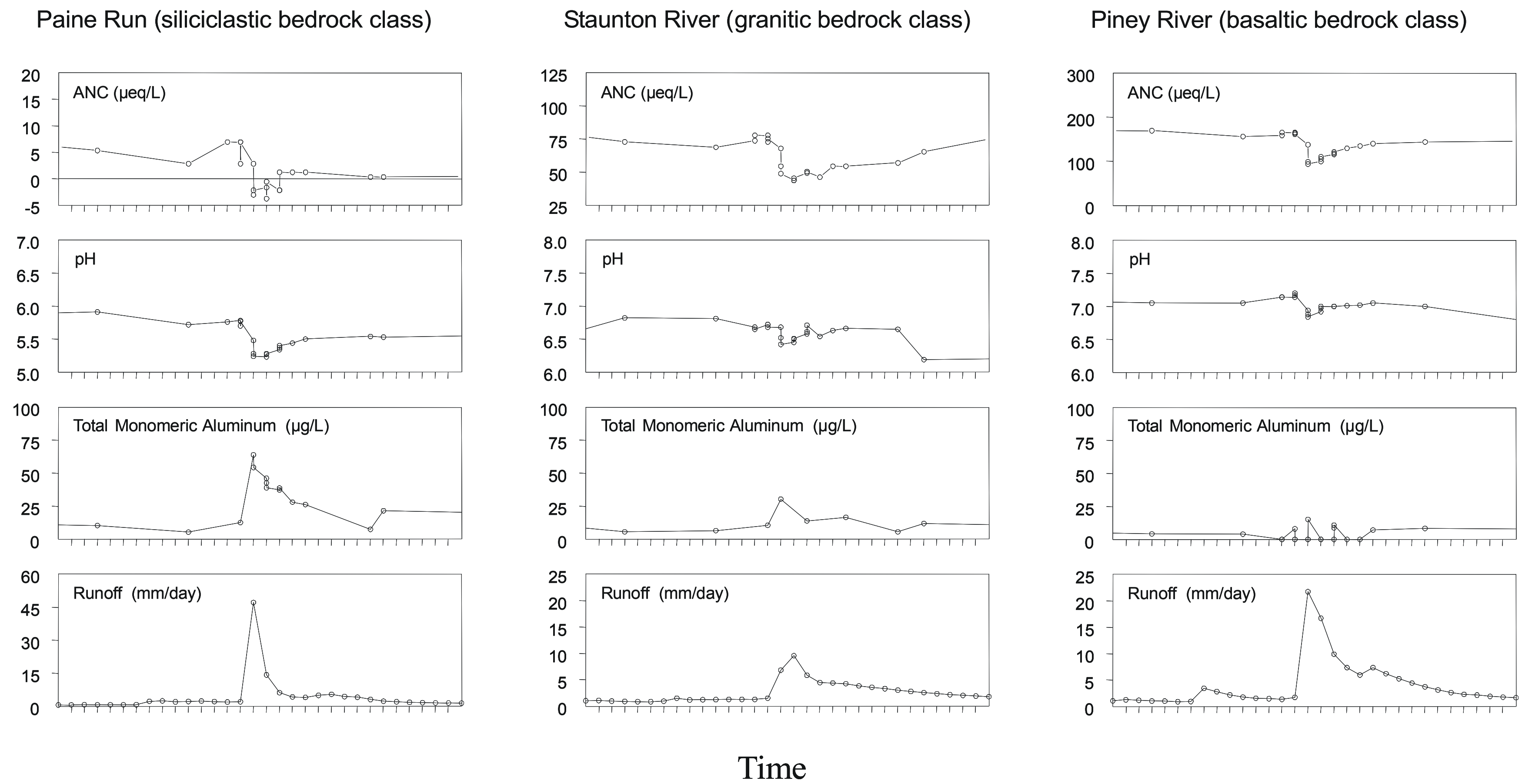



Figure VI-20. Decrease in ANC and pH and increase in dissolved aluminum in response to a sharp increase in streamflow in three watersheds within SHEN during a hydrological episode in 1995. The watersheds were selected to be representative of the three geologic sensitivity classes within the park. Data are shown for the month of January, 1995.

This spatial pattern in streamwater ANC variability within the SWAS watersheds is similar for streams on all three major bedrock types. The implications may be greatest, however, for streams on granitic bedrock. Although these streams usually have ANC and pH values above the range of values commonly associated with harm to fish and other aquatic life, adverse effects may occur periodically due to episodic mobilization of Al from the more acidic portions of the watersheds.

In general, pre-episode ANC is a good predictor of minimum episodic ANC and also a reasonable predictor of episodic ΔANC. Higher values of pre-episode ANC lead to larger ΔANC values, but minimum ANC values of such streams are generally not especially low. Lowest minimum ANC values are reached in streams that have low pre-episode ANC, but the ΔANC values for such streams are generally small.

Webb et al. (1994) developed an approach to calibration of an episodic acidification model for VTSSS long-term monitoring streams in western Virginia that was based on the regression method described by Eshleman (1988). Median, spring quarter ANC concentrations for the period 1988 to 1993 were used to represent chronic ANC, from which episodic ANC was predicted. Regression results were very similar for the four lowest ANC watershed classes, and they were therefore combined to yield a single regression model to predict the minimum measured ANC from the chronic ANC. Extreme ANC values were about 20% lower than chronic values, based on the regression equation:

$$ANC_{min} = 0.79\ ANC_{chronic} - 5.88 \quad (r^2=0.97;\ \text{se of slope}=0.02,\ p\leq 0.001)$$

Because the model was based on estimation of the minimum ANC measured in the quarterly sampling program, it is likely that the true minimum ANC values were actually somewhat lower than 20% below the measured chronic ANC. Nevertheless, regression approaches for estimation of the minimum episodic ANC of surface waters, such as was employed by Webb et al. (1994) for western Virginia, provide a basis for predicting future episodic acidification. It must be recognized, however, that future episodic behavior might vary from current behavior if chronic conditions change dramatically.

Results from the U.S. EPA's Episodic Response Project demonstrated that episodic acidification can have long-term adverse effects on fish populations. Streams with suitable chemistry during low-flow, but low pH and high Al levels during high flow, had substantially lower numbers and biomass of brook trout than were found in non-acidic streams (Wigington et al. 1996). Streams having acidic episodes showed significant mortality of fish. Some brook trout avoided exposure to stressful chemical conditions during episodes by moving downstream or into areas with higher pH and lower Al. This movement of brook trout only partially mitigated the adverse effects of episodic acidification, however, and was not sufficient to sustain fish biomass or species composition at levels that would be expected in the absence of acidic episodes. These findings suggested that stream assessments based solely on chemical measurements during low-flow conditions will not accurately predict the status of fish populations and communities in small mountain streams unless some adjustment is made for episodic processes (Baker et al. 1990b, Baker et al. 1996, Wigington et al. 1996, Sullivan 2000).

Thus, episodic acidification of streams in SHEN can be attributed to a number of causes, including dilution of base cations and increased concentrations of sulfuric, nitric, and organic acids (Eshleman et al. 1995, Hyer et al. 1995). For streams having low pre-episodic ANC, episodic decreases in pH and ANC and increases in toxic Al concentrations can have adverse impacts on fish populations. Not all of the causes of episodic acidification are related to acidic deposition. Base-cation dilution and increase in organic acid anions during high-flow conditions are natural processes. The contribution of nitric acid, indicated by increased $NO_3^-$ concentrations, has evidently been (at least for streams in the park) related to forest defoliation by the gypsy moth (Webb et al. 1995, Eshleman et al. 1998). However, significant contributions of sulfuric acid, indicated by increased $SO_4^{2-}$ concentrations during episodes in some streams, is an effect of atmospheric deposition and the dynamics of S adsorption on soils (Eshleman and Hyer 2000).

## C. VEGETATION

### 1. Effects of Ground-level Ozone and Other Gaseous Pollutants

Ozone ($O_3$) is a photochemical oxidant that occurs naturally in the earth's troposphere. Concentrations of $O_3$ generally increase during the day in a pattern that parallels photosynthetic activity of plants, although this may not be true at high elevation or under conditions of long-range transport. Ozone enters the leaf through stomata during the normal uptake of carbon dioxide and loss of water. Inside the leaf, $O_3$ catalyzes the formation of free radicals which oxidize membranes and damage the photosynthetic apparatus. Although repair of injured tissues takes place, plants are generally unable to completely reverse the effects of exposure to high concentrations of $O_3$, and visible injury and/or growth losses frequently occur.

In 1996, after a review of the scientific literature (U.S. EPA 1996a), the staff of the EPA Office of Air Quality Planning and Standards concluded that the existing secondary National Ambient Air Quality Standards (NAAQS) for $O_3$ did not provide adequate protection for vegetation (U.S. EPA 1996b). They recommended that if the EPA Administrator found that additional protection provided by the proposed change to the primary NAAQS was not sufficient to protect vegetation, that a secondary standard of 25 to 38 ppm·hr (parts per million per hour) 3-month, 12-hour SUM06 be considered[1]. They stated that the lower end of the range would "provide increased protection against effects to vegetation and ecosystem resources in Class I and other areas" (U.S. EPA 1996b). In 1997-1999, the 3-month, 12-hour SUM06 at Big Meadows in SHEN was 28, 52, and 43 ppm·hr respectively, in all cases above the most protective level recommended, and in two of three years, greater than the upper limit recommended by EPA staff. After consideration, the EPA Administrator determined that additional protection, above and beyond that provided by a new, more stringent primary standard to protect human health, was not needed.

*a. Visible Injury Caused by Ground-level Ozone*

Ozone injury is commonly observed on sensitive vegetation in the eastern United States and in southern California. It takes on a special significance in national parks where it is an obvious sign of adverse impact due to air pollution. However, visible injury has rarely been related to quantitative changes in growth or function of a plant, so questions regarding the importance of visible injury to the health and vitality of the forest remain unanswered.

Some plants, such as milkweed (*Asclepias* spp.), black cherry (*Prunus serotina* Ehrh.), and yellow poplar (*Liriodendron tulipifera* L.), are sensitive to $O_3$ and may be injured at exposure to less than 15 ppm·hr, 3-month SUM06. The injury generally is manifested as a purple to brown stipple on the upper surface of the leaf (Figure VI-21). Under severe conditions, the injury may become necrotic and cause flecking on the leaf. The current NAAQS for $O_3$ will not protect all

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[1] To calculate this metric, all ozone concentrations $\geq 0.06$ parts per million (ppm) that occur during 0800-2000 local time in the months of June, July, and August are summed. The 5 month SUM06 used later in this report is calculated in the same manner, but over the growing season months May through September.

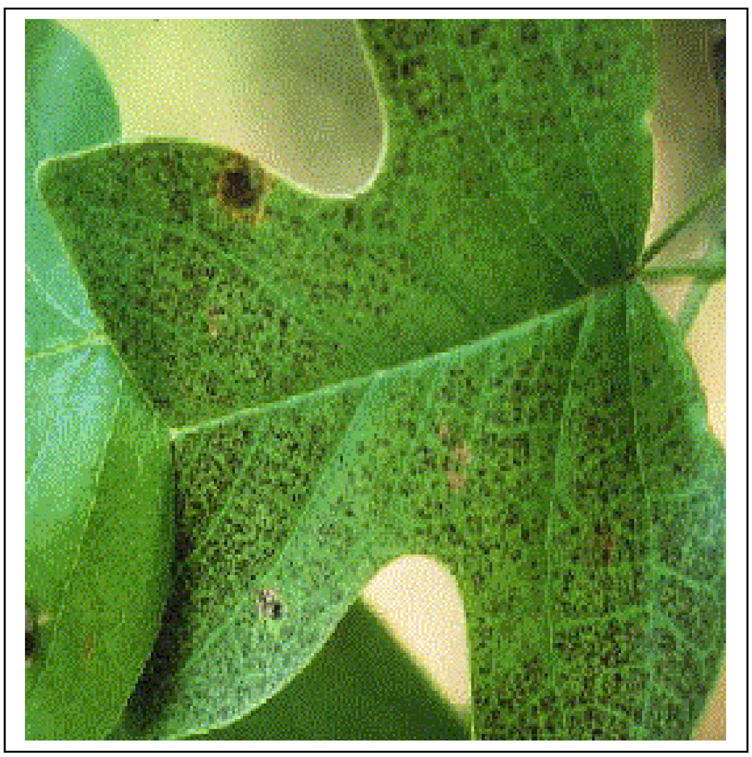

Figure VI-21. Visible injury (purple stippling) caused by ozone on milkweed (top) and yellow poplar (bottom) at SHEN.

sensitive plants from visible injury caused by $O_3$. Sensitive plants in SHEN are likely to continue to show injury well into the future.

In general, visible injury is directly related to the level of $O_3$ exposure (Skelly et al. 2001). If exposures decrease under future air pollution control scenarios, there should be some amelioration of current levels of visible injury. However, if $O_3$ concentrations increase in the lower atmosphere, one would expect not only an increase in the severity of injury to sensitive species but also an increase in the number of species injured. In addition, based on the modeling results reported in Section VII, increased effects on growth might also be expected for some species.

*b. Effects of Sulfur and Nitrogen Oxides*

Some species of plants that occur at SHEN, including raspberry, ragweed, aster, and birch, are reported to be sensitive to $SO_2$ (National Academy of Sciences [NAS] 1978), but it is unlikely that phytotoxic concentrations of the pollutant exist in the park. Similarly, it is unlikely that phytotoxic concentrations of gaseous N occur in SHEN.

Direct vegetation effects of oxides of N in a gaseous form are rare because the toxicities of these compounds are less than those of other pollutants. By far the most important effects of these compounds in SHEN are as precursors to $O_3$ and other photochemical oxidants (c.f., NAS 1977), as fertilizers, and as components of acidic deposition.

## 2. Sensitivity of Plant Species in SHEN

There are a number of plant species that occur within SHEN that are known to be sensitive to $O_3$ effects on foliage at $O_3$ concentrations found within the park (Table VI-11). However, not much is known about the effects of $O_3$ on the growth of trees in SHEN, primarily because it is difficult to work with large trees and the response of seedlings may not be indicative of the response of mature trees (see the discussion below of effects on seedlings). Generally, sugar maple is considered insensitive (Laurence et al. 1996) whereas yellow poplar, red maple (*Acer rubrum*), and red oak (*Quercus rubra* L.) might be considered intermediate (U.S. EPA 1996b). Black cherry is considered to be sensitive in terms of visible injury, but may be less so when evaluating growth responses (Weinstein et al. 2001). Little experimental data is available

Table VI-11. List of plant species in SHEN known to be sensitive to visible injury on foliage from ozone exposure levels found within the park.[a] This list is for general guidance only and does not provide an indication of relative sensitivity to ozone effects on plant growth and vigor.

| Scientific Name | Common Name |
|---|---|
| **SPECIES VERY SENSITIVE TO OZONE EXPOSURE PRESENT AT THIS SITE** | |
| Ailanthus altissima (P. Mill.) Swingle | tree of heaven |
| Apocynum androsaemifolium L. | spreading dogbane |
| Asclepias exaltata L. | poke milkweed |
| Asclepias quadrifolia Jacq. | fourleaf milkweed |
| Asclepias syriaca L. | common milkweed |
| Aster acuminatus Michx. | Oclemena acuminata |
| Aster macrophyllus L. | bigleaf aster |
| Aster puniceus L. | purplestem aster |
| Aster umbellatus P. Mill. | Doellingeria umbellata |
| Fraxinus americana L. | white ash |
| Fraxinus pennsylvanica Marsh. | green ash |
| Liquidambar styraciflua L. | sweetgum |
| Liriodendron tulipifera L. | tuliptree |
| Parthenocissus quinquefolia (L.) Planch. | Virginia creeper |
| Pinus pungens Lamb. | table mountain pine |
| Platanus occidentalis L. | American sycamore |
| Populus tremuloides Michx. | quaking aspen |
| Prunus pensylvanica L. f. | pin cherry |
| Prunus serotina Ehrh. | black cherry |
| Rhus copallina L. | dwarf sumac |
| Rubus allegheniensis Porter | Allegheny blackberry |
| Rudbeckia hirta L. | blackeyed Susan |
| Rudbeckia laciniata L. | cutleaf coneflower |
| Sambucus canadensis L. | Sambucus nigra ssp. canadensis |
| Sassafras albidum (Nutt.) Nees | sassafras |
| Vitis labrusca L. | fox grape |
| **SPECIES SLIGHTLY SENSITIVE TO OZONE EXPOSURE PRESENT AT THIS SITE** | |
| Acer negundo L. | boxelder |
| Acer rubrum L. | red maple |
| Betula alleghaniensis Britt. | yellow birch |
| Betula populifolia Marsh. | gray birch |
| Bromus tectorum L. | cheatgrass |
| Cercis canadensis L. | eastern redbud |
| Cornus florida L. | flowering dogwood |
| Pinus virginiana P. Mill. | Virginia pine |
| Rhus glabra L. | smooth sumac |
| Rhus typhina L. | Rhus hirta |
| Robinia pseudoacacia L. | black locust |
| Symphoricarpos albus (L.) Blake | common snowberry |
| Tilia americana L. | American basswood |
| Verbesina occidentalis (L.) Walt. | yellow crownbeard |

[a] This information was provided by Bruce Nash, NPS Natural Resources Information Division, 1999

regarding the response of white ash (*Fraxinus americana*; reported sensitive based on visible injury in the 1960s), chestnut oak (*Quercus prinus* L.), or basswood (*Tilia americana* L.).

In a recent report, Skelly et al. (2001) estimated the extent of visible foliar injury on black cherry, red maple, yellow poplar, and white ash growing in open-top chambers with ambient air in Pennsylvania. In general, they found black cherry to be most sensitive, with injury also occurring on yellow poplar and red maple. White ash was not injured. They were not able to detect $O_3$-induced changes in radial growth of the trees.

Field plots and open-top chambers were established in Big Meadows in SHEN in 1979 to investigate the effects of $O_3$ on tree seedlings. Studies conducted from 1979 to 1981 suggested that ambient levels of $O_3$ caused foliar injury on seedlings of yellow poplar, green ash (*Fraxinus pennsylvanica*), and sweetgum (*Liquidambar styraciflua*), as well as reduced average height growth of yellow poplar, green ash, black locust (*Robinia pseudoacacia*), Virginia pine (*Pinus virginiana*), Eastern white pine (*Pinus strobus*), table mountain pine, (*Pinus pungens*), and Eastern hemlock (*Tsuga canadensis*; Duchelle et al. 1982). It must be recognized, however, that open-top chambers might result in better height growth due to reduced wind stress, so the results of such experiments may not necessarily reflect $O_3$ exposure effects. A concurrent study found that ambient $O_3$ concentrations reduced above-ground biomass production of native vegetation compared to charcoal-filtered air (Duchelle et al. 1983).

Foliar injury surveys were conducted on five native plant species in SHEN in 1982. Three of the five species (virgin's bower [*Clematis virginiana*], black locust, and wild grape [*Vitis* sp.]) displayed increased injury with increased elevation (Winner et al. 1989).

In 1991, trend plots of the $O_3$-sensitive hardwoods yellow poplar, black cherry, and white ash were established near the ambient $O_3$ monitors at Dickey Ridge, Big Meadows, and Sawmill Run in the park. Marked trees in each plot were evaluated for foliar $O_3$ injury in 1991, 1992, and 1993 (Hildebrand et al. 1996). Black cherry and white ash exhibited increased foliar injury with increased $O_3$ exposure across all three sites and at each site across all years of study. Whereas the amount of foliar injury on yellow poplar at Dickey Ridge corresponded well with $O_3$ exposure, there was no correlation for this species at the Big Meadows or Sawmill Run sites. The authors speculated the lack of correlation for yellow poplar at Big Meadows and Sawmill Run may have been due to extremes in moisture availability at the two sites. Hildebrand et al. (1996) concluded that cumulative $O_3$ statistics, such as SUM06 and W126 (the sum of hourly average $O_3$ concentrations using a sigmoidal weighting function), best represented foliar injury observations, particularly for black cherry, during the period of study.

Thus, $O_3$-induced foliar injury has been observed on a number of species in SHEN since the early 1980s. The amount of foliar injury on black cherry, in particular, correlated well with cumulative $O_3$ exposures. Subsequent data showed that $O_3$ concentrations generally increased in the park throughout the 1990s, which suggests that $O_3$ injury continued.

### 3. Acidification Effects

Deposition of both S and N are of concern with respect to potential acidification effects on forest vegetation throughout the Appalachian Mountains, including within SHEN. However, the forest resource in this region at greatest risk is the spruce-fir ecosystem that is found at high elevation, and that has limited occurrence within SHEN. This resource is of greatest concern because it:

1) contains a tree species (red spruce [*Picea rubens*]) that is highly sensitive to damage by acidification,
2) exhibits soil properties that render it particularly sensitive to soil acidification, including low pH and base saturation, and shallow rooting zone, and
3) receives very high levels of cloud deposition, and therefore total deposition, of S and N at some locations.

Potentially sensitive spruce-fir forest resources are found at high elevation (generally above about 1,370 m) in the southern Appalachian Mountains, including some areas of West Virginia and Virginia. There are small (~18 ha) relic populations of red spruce in SHEN at Limberlost and Hawksbill Peak (NPS 1981). These populations are likely under considerable natural stress and may be more susceptible to the effects of high S and/or N deposition than other forest types in SHEN.

In general, deciduous forest stands in the eastern United States do not progress toward N-saturation as rapidly or as far as coniferous stands. Decreased growth and increased mortality have more commonly been observed in coniferous stands (Aber et al. 1998). There is no evidence to suggest that the levels of N deposition observed in SHEN should lead to forest decline in the deciduous forests of the park. However, the complex relationships between atmospheric inputs and forest health are nevertheless of concern, especially in view of the demonstrated effects of acidic deposition in some situations on soil acidity, nutrient supply, metal toxicity, and tree growth. It is also not known whether forest ecosystems at SHEN are experiencing subtle effects of elevated N-deposition, and whether, for example, some plant species are favored by the relatively high-N environment at the expense of other species.

Possible mechanisms for acidification impacts on terrestrial ecosystems include soil acidification, increased concentration of Al in soil solution, and decreased availability of base cations. These mechanisms can be inter-related. For example, Lawrence et al. (1995) proposed that the dissolution of Al in the mineral soil by mineral acid anions supplied by acidic deposition ($SO_4^{2-}$, $NO_3^-$) can decrease the availability of $Ca^{2+}$ in the overlying forest floor. This conclusion was based on the results of a survey in 1992 and 1993 of soils in red spruce forests that had been acidified to varying degrees throughout the northeastern United States. The proposed mechanism for $Ca^{2+}$ depletion is as follows. Acidic deposition lowers the pH in the mineral soil, thereby increasing the concentration of dissolved Al in soil solution. Some of the Al is then taken up by tree roots and transported throughout the trees, eventually to be recycled to the forest floor in leaves and branches. Additional dissolved Al is transported to the forest floor by rising water table during wet periods and by capillary movement during dry periods. Because $Al^{3+}$ has a higher affinity for negatively-charged soil surfaces than $Ca^{2+}$, introduction of Al into the forest floor, where root-uptake of nutrients is greatest, causes $Ca^{2+}$ to be displaced from the cation exchange complex, and therefore more easily leached with drainage water (Lawrence et al. 1995, Lawrence and Huntington 1999).

Aluminum is not only toxic to aquatic biota. Aqueous Al is also toxic to tree roots, although much higher concentrations of Al in soil solution are required in order to elicit a toxic response as compared with the toxicity of Al to fish in surface water. Plants affected by high levels of Al in soil solution typically exhibit reduced root growth. Stunting of the root system restricts the ability of the plant to take up water and nutrients (Parker et al. 1989). Calcium is well known as an ameliorant for Al toxicity to roots, as well as to fish. Magnesium, and to a lesser extent the monovalent base cations, $Na^+$ and $K^+$, have also been associated with reduced Al toxicity. Neither the molecular basis for Al toxicity to plant roots nor the basis for the reduction in toxicity found for base cations is well understood. Efforts to estimate critical levels of atmospheric S or N deposition that will protect sensitive forest resources from damage often use the molar ratio of $Ca^{2+}$ to Al in soil solution as an indicator of potential toxic effects. It has been suggested that damaged forest stands often exhibit Ca:Al < 1.0 (Ulrich 1983, Schulze 1989, Sverdrup et al. 1992).

The adverse, soil-mediated effects of acidic deposition are believed to result from increased toxic Al in soil solution and concomitant decreased $Ca^{2+}$ or other base cation concentrations (Ulrich 1983, Sverdrup et al. 1992, Cronan and Grigal 1995). A reduction in the Ca:Al ratio in soil solution has been proposed as an indicator reflecting increased probability of Al toxicity and nutrient imbalances in sensitive tree species. This topic was reviewed in detail by Cronan and Grigal (1995), who concluded that the Ca:Al molar ratio provides a valuable measurement endpoint for identification of approximate thresholds beyond which the risk of forest damage from Al stress and nutrient imbalances increases. Base cation removal in forest harvesting can have a similar effect and can exacerbate the adverse effects of acidic deposition. Based on a critical review of the literature, Cronan and Grigal (1995) estimated that there is a 50% risk of adverse impacts on tree growth or nutrition where soil solution Ca:Al $\leq$ 1.0. Aluminum toxicity to tree roots and associated nutrient deficiency problems are largely restricted to soils having low base saturation. The Ca:Al ratio indicator was recommended for assessment of forest health risks at sites or in geographic regions where the soil base saturation is < 15%, such as is found in siliciclastic and many granitic watersheds in SHEN.

Based on published research findings, it is unlikely that terrestrial ecosystems in SHEN have experienced sufficiently high deposition of S or N so as to cause substantial adverse acidification-related impacts to forests. There are several reasons why such impacts are unlikely. First, the vegetation type that appears to be most susceptible to damage from acidic deposition, spruce-fir forest, is largely absent from SHEN, although there are small relic populations of red spruce. Second, the highest point in the park is only 1,234 m, which is below the elevation at which cloud deposition of S and N has been shown to be a large contributor to total S and N deposition. For example, Sigmon et al. (1989) estimated total warm season cloud deposition at the Pinnacles of SHEN (1,014 m elevation) equal to 0.9, 0.7, and 0.2 kg/ha/mo, respectively, for $SO_4^{2-}$, $NO_3^-$, and $NH_4^+$. These cloud deposition estimates contrast with the estimates by Lindberg et al. (1988) at Great Smoky Mountains National Park (1,740 m elevation) that were more than three-fold higher for $NO_3^-$, eight-fold higher for $SO_4^{2-}$, and five-fold higher for $NH_4^+$ (c.f., Vong et al. 1991). Due to high cloud deposition, total S and N deposition levels are therefore much higher at Great Smoky Mountains than at SHEN. Third, total deposition levels of both S and N are below levels that have been shown to cause adverse impacts on forest ecosystems elsewhere (Tietema and Beier 1995, Dise and Wright 1995, Dise et al. 1998). Fourth, because the forests in SHEN are almost exclusively second growth, subsequent to large-scale timber harvesting and localized agricultural land use prior to park creation, the N-demand of the regrowing forest is likely to be high. This precludes $NO_3^-$ leaching at current N deposition levels in the absence of significant disturbance such as was seen with gypsy moth infestation. Fifth, it is likely that the lower elevation deciduous forests of SHEN, as compared with the high-elevation spruce-fir forests of Great Smoky Mountains, have higher base saturation and soil pH and would therefore not be expected to show the same level of cation deficiency and inorganic Al stress that sometimes characterize the higher elevation sites (Eagar et al. 1996).

Thus, although there is some evidence that spruce forests in the Great Smoky Mountains have experienced adverse effects from N deposition, it is important to note that total N (wet, dry, cloud) deposition at high elevation in the Great Smoky Mountains is considerably higher than is found in SHEN. In addition, the deciduous forests at SHEN are less sensitive to adverse impacts of N deposition. The very high levels of N deposition at some locations in the Great Smoky Mountains are mostly attributable to the high amounts of cloud deposition received in those high elevation areas. As a consequence, the streams that drain undisturbed watersheds in the Great Smoky Mountains exhibit some of the highest recorded $NO_3^-$ concentrations in the United States and also $NO_3^-$ concentrations that can be comparable to or higher than $SO_4^{2-}$ concentrations (U.S. EPA 1993). In contrast, $NO_3^-$ concentrations in SHEN streams are negligible in the absence of insect infestation.

Thus, with respect to the risk factors generally associated with acidification effects on forest vegetation in other areas of the southern Appalachian Mountains, it appears that forests in SHEN are relatively less susceptible to harm. Nonetheless, examination of the available soils information for SHEN watersheds suggests that there may be some risk of adverse effects and that the degree of risk varies spatially within the park. Some acid-base chemistry measurements for soils on siliciclastic bedrock, and to a lesser extent for soils on granitic bedrock, approach or exceed values that have been suggested as thresholds for identification of acid-sensitive forest soils (e.g., base saturation less than 20%, pH less than 4.5; Table VI-4). It is not clear whether forest soils at SHEN will ultimately develop $Ca^{2+}$ deficiency. Soils may stop changing their base cation status before deficiencies develop as deposition levels decline, or weathering rates may be sufficient to maintain adequate cation nutrient supplies.

As discussed previously, Tables VI-4 and VI-5 provide summary data for soils sampled in 2000 at 79 geologically distributed sites in SHEN (Welsch et al. 2001). The range of base saturation values obtained for soils associated with both siliciclastic and granitic bedrock include values in the 10-20% range cited as possible threshold values for incomplete acid neutralization and leaching of Al (Reuss and Johnson 1986, Binkley et al. 1989, Cronan and Schofield 1990). Moreover, the measured soil pH for soils associated with both siliciclastic and granitic bedrock include values in the highly acidic range (pH < 4.5) in which the more-toxic forms of Al often predominate (Binkley et al. 1989).

Elevated Al concentrations in streamwater are often observed during high-runoff conditions in intensively monitored streams (for example, see Figure VI-20), suggesting probable Al mobilization from soils to soil water, although the hydrologic routing of the increased Al is not well understood. As expected, levels of increased Al reflect the observed bedrock-related gradient in soil pH, suggesting that episodically elevated Al concentrations occur in soil water, especially soil water associated with siliciclastic and to a lesser extent granitic bedrock.

Direct measurements of solute composition in SHEN soil waters were obtained using soil water lysimeters installed during 1999-2000 in lower portions of the Paine Run, Staunton River, and Piney River watersheds, representing the park's three major bedrock types (Rice et al. 2001). Table VI-12 provides a summary of the obtained $Ca^{2+}$ and Al concentration data, as well as Ca:Al soil solution molar ratios. In considering this information it should be noted that: (1) the data were not obtained as part of a regular monitoring program, and thus are not expected to account for spatial and temporal variance in park soils; and (2) lysimeter data are highly dependent upon lysimeter design and installation method, which raises questions about data comparability. However, the data do provide preliminary perspective in relation to indices that have been proposed for evaluation of potential soil acidification impacts on vegetation. Binkley et al. (1989) estimated that soil water Al concentrations of 10 to 50 µm/L may affect the growth of sensitive plant species. Median soil solution Al concentrations were well below this range at all sampling locations, although a maximum value of 20.8 µM was reported for the 35 cm depth site in the Paine River watershed (Table VI-12). It has also been observed that uptake of nutrient

Table VI-12. Calcium and aluminum data[a] collected for soil water samples from three watersheds in SHEN[b] during the period 1999-2000.

| Stream | Sample Depth (cm) | n | $Ca^{2+}$ Concentration | | Al Concentration | | Ca:Al Molar Ratio | |
|---|---|---|---|---|---|---|---|---|
| | | | Min. | Median | Median | Max | Min | Median |
| PAIN | 35 | 8 | 10.8 | 49.3 | 5.4 | 20.8 | 2.7 | 4.1 |
| | 66 | 6 | 32.7 | 46.8 | 1.4 | 4.4 | 11.4 | 33.5 |
| | 97 | 10 | 12.3 | 25.2 | 1.4 | 9.1 | 3.6 | 19.1 |
| STAN | 35 | 8 | 67.2 | 89.9 | 0.1 | 0.8 | 133.8 | 503.0 |
| | 66 | 9 | 69.5 | 79.7 | 0.1 | 0.6 | 210.2 | 626.0 |
| | 97 | 4 | 48.8 | 55.2 | 0.0 | 0.2 | 355.2 | 489.0 |
| PINE | 35 | 11 | 42.8 | 74.8 | 0.7 | 4.5 | 9.5 | 110.6 |
| | 66 | 7 | 72.9 | 93.5 | 0.1 | 1.4 | 410.9 | 930.0 |
| | 97 | 12 | 36.2 | 150.3 | 0.5 | 1.9 | 143.0 | 336.0 |

[a] Units are µM
[b] Source of data: Rice et al. 2001

cations can be diminished somewhat at Al concentrations below those required to reduce growth (Binkley et al. 1989).

Examination of the soil lysimeter data for SHEN in relation to the Ca:Al molar ratio threshold of 1.0 (c.f., Cronan and Griegal 1995) suggests that soil water solute concentrations collected in all three watersheds were always above the threshold, and the minimum reported value was 2.7 (Table VI-12). Additional study would be needed to determine the extent to which this response threshold is meaningful and/or might be exceeded for the park's forest soils. However, the mixed hardwood forests that predominate in SHEN are evidently less sensitive to harm from soil acidification than the higher elevation spruce-fir forests located elsewhere in the southern Appalachian Mountains. Nevertheless, in view of the limited available soil and soil water data, the potential for harm in SHEN cannot be ruled-out.